

STUDIES ON DISSOCIATION RATES
OF SOME
LANTHANOID EDTA COMPLEXES

by

Torsten Ryhl

Lund 1971

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AVHANDLING FÖR FILOSOFIE DOKTORSEXAMEN

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Fil lic, Hb

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Chapter 1

INTRODUCTION

The lanthanoids, i.e. the elements No. 57 lanthanum to No. 71 lutetium, form a series of elements of similar properties. The normal charge of their ions is +3. Owing to the shielding of the 5 s and 5 p orbitals, the chemical effects of the successively added 4 f electrons throughout the series are small. Hence, the change of chemical properties within the series depends almost exclusively on the decreasing ionic radius for increasing atomic number.

The lanthanoid ions form strong complexes with many multidentate ligands. Thus, the complexes with ethylenediaminetetraacetate, EDTA, have stability constants, ranging from 10^{15} M^{-1} for lanthanum to 10^{20} M^{-1} for lutetium.¹⁻³

X-ray studies by Hoard et al.⁴ of salts of the type $\text{MLnEDTA} \cdot 6 \text{ H}_2\text{O}$, where $\text{M} = \text{K}, \text{Na}$ or NH_4 and $\text{Ln} = \text{La}, \text{Nd}, \text{Gd}, \text{Tb},$ and Er have shown a coordination structure in which EDTA, acting as a hexadentate ligand, is bonded to the central ion by four oxygen and two nitrogen atoms. The EDTA ligand is located at one side of the central ion, while the opposite side is occupied by coordinated water molecules. A plane, defined by the central ion and the nitrogen atoms, serves as a quasi-mirror plane through the complex. As the radius of the central ion decreases along the series, the lanthanoid ion presumably sinks deeper into the "basket" formed by the ligand molecule, which results in a shortening of the metal-nitrogen distances. Another possible result is a change in the number of coordinated water molecules. Thermodynamic data⁵ also indicate a change in the coordination number, possibly from nine to eight somewhere in the middle of the lanthanoid series. On thermodynamic, spectroscopic, and kinetic grounds, Geier

and Karlen ⁶⁻⁹ have proposed that two kinds of LnEDTA complexes, viz. $\text{Ln}(\text{EDTA})(\text{OH}_2)_3^-$ and $\text{Ln}(\text{EDTA})(\text{OH}_2)_2^-$, are in equilibrium in solution. For the first members of the series up to samarium, the complex with three water molecules predominates, whereas after dysprosium, the two-water complex is favoured.

Reported kinetic investigations. Some investigations have been reported on the kinetics of lanthanoid EDTA complexes. It is generally the dissociation rate, rather than the rate of formation of complexes, which has been studied. Owing to the high stability of the lanthanoid EDTA complexes, it is not possible to study the dissociation by simply diluting a solution. Instead, a second strongly complexing metal ion has to be introduced into the solution, which results in an exchange reaction of the type $\text{LA} + \text{M} \rightleftharpoons \text{L} + \text{MA}$. Reactions of this type are usually catalysed by hydrogen ions.

The following studies have been performed in slightly acid media with isotope exchange methods. Betts et al. ¹⁰ determined the exchange rates for the EDTA complexes of La, Nd, and Yb. Later, rate constants for the following systems have also been reported: Pr and Ce (ref. 11), Lu (ref. 12), Ce and Lu (ref. 13), Ho (ref. 14), Lu (ref. 15), Ce (ref. 16), Ce, Nd, Gd, Tb, and La (ref. 17), and Ce and Eu (ref. 18).

Merbach and Gnägi ¹⁹ studied the kinetics of the ligand exchange of lanthanum and lutetium EDTA complexes in alkaline solutions by NMR line broadening. The rate constants were obtained from more approximate methods of computation than the line shape analysis used in the present work. Studies on mixed EDTA lanthanoid complexes have also been reported. Thus, Geier and Karlen ⁸ have studied the kinetics of association of lanthanoid EDTA complexes to oxyquinoline -5- sulfonate by the temperature jump method. They found changes in the rate determining steps

along the series, supporting the above mentioned suggestion of two differentially hydrated complexes. Brucher and Szilágy²⁰ computed rate constants from spectrophotometric measurements for copper ions exchanging ligands with TbEDTA and TbEDTA glycolate.

Several different rate laws and mechanisms have been suggested in the investigations cited. Most of the papers give only one reaction path, viz. a path, catalysed by hydrogen ions, giving a first order term in the rate equation. Furthermore, a decrease in the rate constant along the lanthanoid series has been related to the increasing stability constant.

The aim of the present study. The aim of the present investigation is to determine the dissociation rates and possible reaction mechanisms of some lanthanoid EDTA complexes with methods other than isotope exchange reactions. The suggested existence of two types of EDTA complexes, containing two or three water molecules, might be reflected in the rate constants of the dissociation. One would also expect a hydroxide ion catalysis of the dissociation of the complex, since complexes are known which contain both EDTA and hydroxide as ligands. This has not been examined in the previous studies.

Experimental methods. As already mentioned, it is necessary to use a second strongly complexing metal ion to study the rate of dissociation of the complexes. For this purpose either copper ions or, in some case, a second lanthanoid ion has been used.

At concentrations around 10^{-3} M, the reactions of Cu, Yb, and Er complexes proceed rather slowly. Hence, the change in the copper EDTA concentrations could be followed by a conventional spectrophotometric method. Because of the small absorption coefficients of the f-f spectra and the nearly identical ligand spectra in the UV region between the different lanthanoid complexes, the reaction between

ytterbium ions and the europium EDTA complex is difficult to follow by spectrophotometric methods. However, the differences in the polarographic half-wave potentials are large enough to allow the reaction to be followed by measuring the diffusion current of the free europium ion. The half-life of this reaction is a few minutes or less, if proper concentrations are chosen.

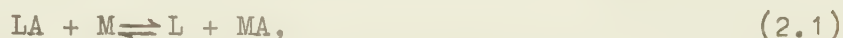
With copper as exchanging metal, the Nd, Pr, and La systems could be measured by a stopped-flow method for half-lives down to a few ms. By the same technique, CuEDTA could be studied by using lanthanum ions as ligand acceptor.

Because of hydrolysis, it is not possible to use an excess of free metal ions in the alkaline range. By the NMR line broadening technique, which uses an excess of free ligand and no second exchanging metal ion, it is possible to determine the hydroxide catalysed rate of dissociation for the diamagnetic lanthanum EDTA complex. The NMR spectra can also give some information about the symmetry and bondings of the complex.

Chapter 2

THE KINETIC MODEL

General description of the model. This model, which is in accordance with reactions discussed by Margerum ²¹, has been proposed by Ekström, who gives a more detailed description elsewhere ²². It describes possible reactions of a ligand exchange between two different metal ions, according to the over-all reaction

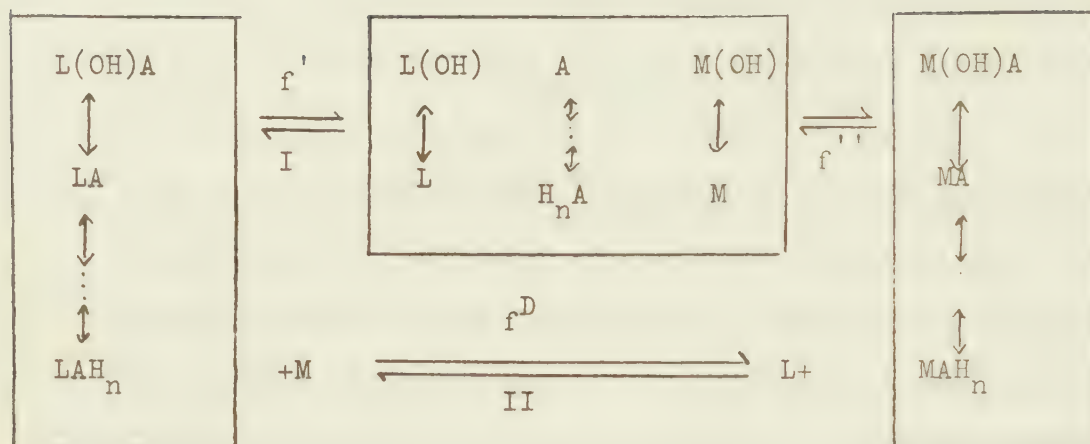


where A denotes the ligand and L and M the two metal ions. Catalysis by hydrogen and hydroxide ions has been included in the model. The ligand is considered to have a multidentate character. Mixed complexes, owing to species used as buffers, are excluded in this short description.

Two different reaction paths are taken into account, viz.

- i) a primary rate determining dissociation of the complex LA, followed by an association of the ligand A to the exchanging metal ion M, and
- ii) a direct substitution reaction between M and the complex LA passing over an intermediate species LAM to the products L and MA.

If the metal ion L has a high coordination number compared to the multidentate ligand A, which itself has possibilities to form species of the type HA, H₂A, H_nA, there exist several possibilities to form mixed complexes, such as L(OH)A, LAH, LAH_n. The distribution of L over these species depends on the acidity of the solution. The exchanging metal ion M may also have similar possibilities to form mixed complexes. The situation is described in the following reaction scheme.

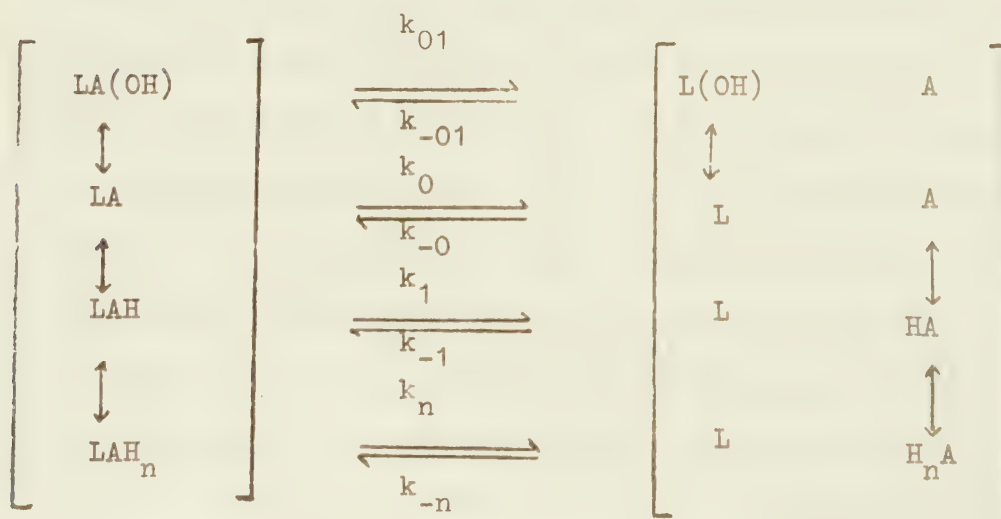


In this scheme $\leftrightarrow$ denotes a fast equilibrium, f' a function of the hydrogen ion concentration and of the rate constants for the dissociation of the various LA complexes, f'' the corresponding function for the MA complexes. f^D is a function of the hydrogen ion concentration and of the rate constants for the direct substitution reaction.

Deduction of the rate law

The rate of disappearance of LA along path I..

The following reaction scheme is regarded:



All species enclosed in the left brackets are in fast equilibrium with each other. Each of them dissociates to the products within the right brackets. Thus, the rate of disappearance of all complexes containing L and A is

$$\frac{-d([L(OH)A] + [LA] + \dots [LAH_n])}{dt} = \frac{-dC'_{LA}}{dt} \quad (2.2)$$

$$= k_{01}[L(OH)A] - k_{-01}[L(OH)][A] + k_0[LA] - k_{-0}[L][A] + k_1[LAH] - k_{-1}[L][HA] + \dots + k_n[LAH_n] - k_{-n}[L][H_nA],$$

where C'_{LA} denotes the sum of the concentrations of all types of LA complexes at the time t. By introducing the following equilibrium constants

$$K_{LAH_n} = \frac{[LAH_n]}{[LA][H]^n} ; \quad \beta_L = \frac{[LA]}{[L][A]} ; \quad (2.3)$$

$$K_{L(OH)A} = \frac{[L(OH)A][H]}{[LA]} ; \quad K_{L(OH)} = \frac{[L(OH)][H]}{[L]} ;$$

$$\text{and } \gamma_n = \frac{[H_nA]}{[A][H]^n}$$

and remembering that

$$\frac{k_n}{k_{-n}} = \frac{[L][H_nA]}{[LAH_n]} \quad \text{and} \quad \frac{k_{01}}{k_{-01}} = \frac{[L(OH)][A]}{[L(OH)A]} \quad (2.4)$$

equation(2.2) can be written as

$$- \frac{d[LA]}{dt} (1 + K_{L(OH)A} \cdot \frac{1}{[H]} + \dots + K_{LAH_n} [H]^n) \quad (2.5)$$

$$= (k_{01} K_{L(OH)A} \cdot \frac{1}{[H]} + k_0 + \dots + k_n K_{LAH_n} [H]^n) [LA]$$

$$- (k_{01} K_{L(OH)A} \cdot \frac{1}{[H]} + k_0 + \dots + k_n K_{LAH_n} [H]^n) \beta_L [L][A];$$

Hence

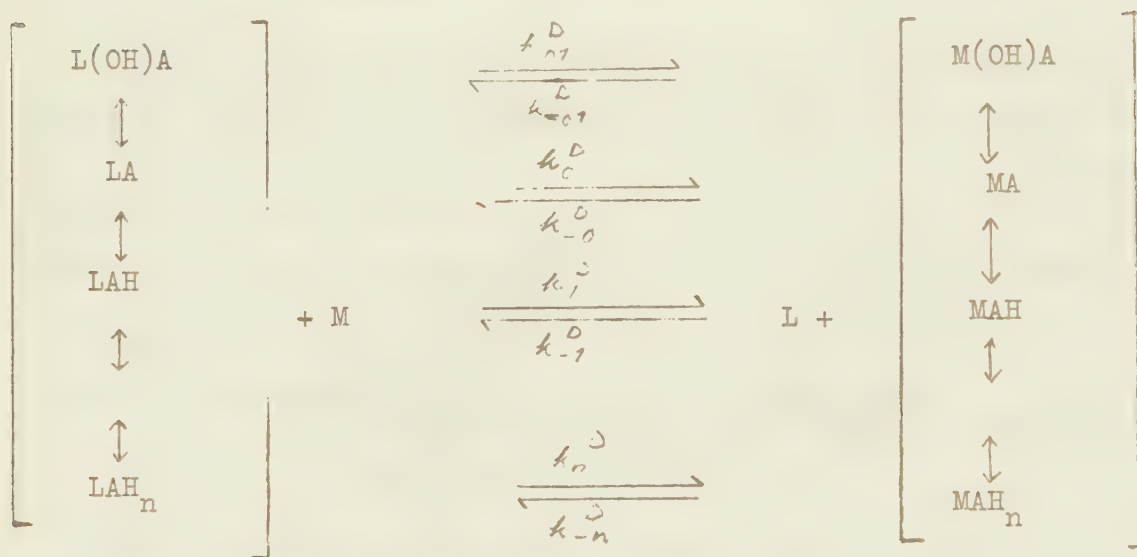
$$-\frac{d[LA]}{dt} \cdot f_o = f'([LA] - \beta_L[L][A]) \quad (2.6)$$

$$\text{where } f_o = 1 + K_{L(OH)A} \frac{1}{[H]} + \dots + K_{LAH_n} [H]^n$$

$$\text{and } f' = k_{o1} K_{L(OH)A} \frac{1}{[H]} + k_o + \dots + k_n K_{LAH_n} [H]^n$$

The rate of disappearance of LA along path II.

With the reaction scheme for this path



the rate equation for disappearance of the LA complexes is

$$-\frac{d([L(OH)A] + \dots + [LAH_n])}{dt} = -\frac{dC'_{LA}}{dt} = \quad (2.7)$$

$$= k_{o1}^D [L(OH)A][M] - k_{-o1}^D [L][M(OH)A] +$$

$$+ k_o^D [LA][M] - k_{-o}^D [L][MA] + \dots$$

$$\dots + k_n^D [LAH_n][M] - k_{-n}^D [L][MAH_n];$$

Using corresponding equilibrium constants as for path I equation

(2.7) results in

$$-\frac{d[LA]}{dt} \cdot f_0 = (k_{O1}^D K_{L(OH)A} \frac{1}{[H]} + k_O^D + \dots + k_n K_{LAH_n} [H]^n) [LA][M] - \quad (2.8)$$

$$-\frac{\beta_L}{\beta_M} (k_{O1}^D K_{L(OH)A} \frac{1}{[H]} + k_O^D + \dots + k_n K_{LAH_n} [H]^n) [MA][L],$$

which gives

$$-\frac{d[LA]}{dt} \cdot f_0 = f^D ([LA][M] - \frac{\beta_L}{\beta_M} [MA][L]), \quad (2.9)$$

where f_0 is given above and

$$f^D = k_{O1}^D K_{L(OH)A} \frac{1}{[H]} + k_O^D + \dots + k_n^D K_{LAH_n} [H]^n.$$

The complete rate law. The total rate of disappearance of LA complexes is the sum of the rates along paths I and II. Thus

$$-\frac{dC'_{LA}}{dt} = -\frac{d[LA]}{dt} \cdot f_0 = f'([LA] - \beta_L [L][A]) + f^D([LA][M] - \frac{\beta_L}{\beta_M} [MA][L]) \quad (2.10)$$

The rate of formation of all types of MA complexes is equal to the rate of disappearance of all types of LA complexes.

$$-\frac{dC'_{LA}}{dt} = \frac{dC'_{MA}}{dt};$$

This steady state approximation means that

$$\frac{d[A]}{dt} = 0; \quad (2.12)$$

Furthermore, it is assumed that the hydrogen ion concentration does not change during the reaction, i.e.

$$\frac{d[H]}{dt} = 0; \quad (2.13)$$

The steady state condition implies

$$f'([LA] - \beta_L [L][A]) + f^D([LA][M] - \frac{\beta_L}{\beta_M}[MA][L]) = \quad (2.14)$$

$$- f''([MA] - \beta_M [M][A]) + f^D([M][LA] - \frac{\beta_L}{\beta_M}[MA][L]),$$

where f'' is analogous to f' , but valid for MA instead of LA.

Combination of equations (2.10) and (2.14) gives

$$-\frac{d[LA]}{dt} \cdot f_o = \left(\frac{f' f'' \beta_M}{f' \beta_L [L] + f'' \beta_M [M]} + f^D \right) ([LA][M] - \frac{\beta_L}{\beta_M} [L][MA]); \quad (2.15)$$

At equilibrium, the total concentration of all species containing L and A is

$$C_{LA} = [LA]_{eq} \cdot f_{LA} \quad (2.16)$$

and the corresponding concentration of L is

$$C_L = [L]_{eq} \cdot f_L \quad (2.17)$$

where f_{LA} and f_L are functions of equilibrium constants and the hydrogen ion concentration (analogous to f_o). At a time t the concentrations of the different species differ from the corresponding equilibrium concentrations by the quantities x_i , defined by

$$[LA] = [LA]_{eq} + x_{LA}; \quad [L] = [L]_{eq} - x_L; \quad (2.18)$$

$$[MA] = [MA]_{eq} - x_{MA}; \quad [M] = [M]_{eq} + x_M;$$

$$C'_{LA} = C_{LA} + x; \quad C'_{MA} = C_{MA} - x;$$

If x is expressed in terms of the various x_i and inserted in equation (2.15) one obtains

$$\frac{dx}{dt} = \left(\frac{f' \cdot f''}{f' \beta_L \frac{C_L}{f_L} \left(1 - \frac{x}{C_L}\right) + f'' \beta_M \frac{C_M}{f_M} \left(1 + \frac{x}{C_M}\right)} + \frac{f^D}{\beta_M} \right) \quad (2.19)$$

$$\cdot \left(\beta_M \frac{C_{LA} + C_M}{f_{LA} \cdot f_M} + \beta_L \frac{C_L + C_{MA}}{f_L \cdot f_{LA}} + x \frac{\beta_M}{f_M \cdot f_{LA}} \left(1 - \frac{C_M \cdot C_{LA}}{C_L \cdot C_{MA}}\right) \right) \cdot x$$

If this equation is integrated the result is

$$\ln \frac{x}{x_0} + \frac{Q_1 - Q_2}{Q_2 - Q_3} \ln \frac{1 + Q_2 x}{1 + Q_2 x_0} - \frac{Q_1 - Q_3}{Q_2 - Q_3} \ln \frac{1 + Q_3 x}{1 + Q_3 x_0} =$$

$$- k_{\text{obs}} \cdot t \quad (2.20)$$

where

$$k_{\text{obs}} = \left(\frac{f'}{1 + \frac{f'}{f''} \delta_1} + f^D \frac{C_M}{f_M} \right) \frac{1 + \delta_2}{f_{LA}},$$

$$Q_1 = \frac{1 - \frac{f'}{f''} \frac{\beta_L}{\beta_M} \frac{f_M}{f_L}}{C_M + C_L \frac{f'}{f''} \frac{\beta_L}{\beta_M} \frac{f_M}{f_L}}$$

$$Q_2 = \frac{1 - \frac{f_{LA}}{f_{MA}} \frac{\beta_L}{\beta_M} \frac{f_M}{f_L}}{C_M + C_{LA} + (C_L + C_{MA}) \frac{f_{LA}}{f_{MA}} \frac{\beta_L}{\beta_M} \frac{f_M}{f_L}},$$

$$Q_3 = \frac{1 - \frac{f'}{f''} \frac{\beta_L}{\beta_M} \frac{f_M}{f_L}}{C_M + C_L \frac{f'}{f''} \frac{\beta_L}{\beta_M} \frac{f_M}{f_L} + f_M \frac{f'}{f^D}},$$

$$\delta_1 = \frac{\beta_L}{\beta_M} \cdot \frac{C_L}{C_M} \cdot \frac{f_M}{f_L},$$

and

$$\delta_2 = \frac{C_{LA}}{C_M} + \frac{\beta_L}{\beta_M} \frac{C_L + C_{MA}}{C_M} \cdot \frac{f_M}{f_L} \frac{f_{LA}}{f_{MA}}.$$

If x is small, equation (2.20) reduces to (2.21)

$$\ln \frac{x}{x_0} = -k_{\text{obs}} t.$$

Thus, from measurements of $k_{\text{obs}} = f([H])$ for the LA system, using M as the exchanging metal ion, and of $k_{\text{obs}} = f([H])$ for the MA system, using L as the exchanging metal ion, it is possible to calculate f' and f^D for both systems by an iterative procedure.

Chapter 3

EXPERIMENTAL

Chemicals. All chemicals were of analytical grade. Standard solutions of YbCl_3 , ErCl_3 , EuCl_3 , NdCl_3 , PrCl_3 , LaCl_3 , and CuCl_2 were prepared by dissolving the corresponding oxides (from Potash & Chemical Corp.) in hydrochloric acid. The solutions were standardized with EDTA, using xylenorange for the lanthanoids and glycine thymol blue for the copper as indicators. Ethylenediaminetetraacetic acid was prepared from a solution of the disodium salt, acidified by hydrochloric acid. The precipitate was washed and dried. A stock solution was prepared by dissolving a weighed amount of the acid in a sodium hydroxide solution (c.f. e.g. Schwarzenbach²³). Buffer solutions were prepared from acetic acid and sodium hydroxide. A stock solution of potassium chloride was made by dissolving the weighed amount of dried salt. The solution was standardized by titration with silver nitrate.

The medium and temperature. All measurements were made at 25.0 ± 0.1 °C and at the ionic strength 0.5 M, except for the NMR measurement, where the ionic strength 1.0 was used in the kinetic investigation and the temperature was 44.9 ± 0.3 °C. The ionic strength for each of the solutions S and T (see below) was adjusted to 0.5 M by potassium chloride. The solutions contained 12.5 mM sodium acetate and varying amounts of acetic acid as buffer.

The use of buffer solutions. The lanthanoid EDTA complexes have a rather marked affinity to hydrogen ions, with association constants in the range $100 - 1\,000\text{ M}^{-1}$ 17,24. To avoid considerable concentrations of protonated complexes, the investigation has to be carried out at $\text{pH} > 3$. In order to achieve controlled pH values in this region, a buffer must be used. A mixture of 12.5 mM sodium acetate and varying

amounts of acetic acid was chosen as buffer. Such a buffer has only a small effect on the rate of the reaction. (Chapter 6.)

The reactions were performed by mixing two solutions, one containing the metal of the investigated system and the other the exchanging metal. As a rule, only one of the solutions contained the buffer. No differences in the observed rate constant could be seen, whether the buffer was in only one of the solutions or in both of them before mixing. No foreign buffer was used in the NMR measurements.

Determination of the hydrogen ion concentration. The hydrogen ion concentration of the solutions was determined by measuring the emf of the following cell

Ag, AgCl	0.499 M KCl	$[\text{H}^+]_x$	glass
	1.000 mM HCl	I = 0.5 M	electrode

The solutions in the reference electrode vessel contained known concentrations of hydrogen ions around 1 mM. The diffusion potentials were negligible. The same cell was used in the NMR investigation, but with ionic strengths of 1.0 or 0.2 M instead of 0.5 M.

Chapter 4

SPECTROPHOTOMETRIC MEASUREMENTS

The rates of dissociation of the copper, erbium, and ytterbium EDTA complexes were measured by a spectrophotometric method.

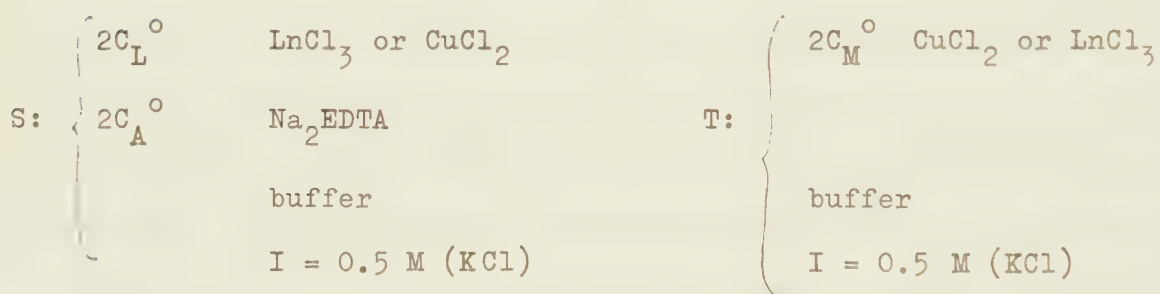
Two solutions, S and T, were thermostated at 25.0 °C and mixed rapidly. (The mixing time was less than 5 s). For the copper system the two solutions were mixed with two calibrated syringes directly into a thermostated cuvette, whereas for the two lanthanoid systems the solutions were mixed into a reaction vessel. Samples from this vessel were then taken at different time intervals and measured by a Zeiss PMQ II spectrophotometer, equipped with a Solatron digital voltmeter LM 142.02, from which the transmittance of the copper EDTA complex was read.

Because of the small total concentration, it was necessary to perform the measurements in the UV region (wave length 280-300 nm), where the molar light absorptivity is high. In the two lanthanoid systems, with an excess of copper as exchanging metal, a marked photocatalytic effect was observed. It is well known that many copper complexes exhibit photolysis in the UV region²⁵. The transmittance of each sample was generally measured after 10 s in the light path. In order to check that this procedure gave k_{obs} -values unaffected by the photocatalytic effect, the following procedure was applied for some runs. By means of a recorder connected to the spectrophotometer, the transmittance for each sample was followed for about 30 s and extrapolated to zero time, i.e. the time when the sample had been placed into the light beam of the spectrophotometer. k_{obs} was then evaluated from these extrapolated values.

The same rate constants were obtained with and without this correction. Some experiments were carried out at both 285 and 600 nm. Those at 600 nm were in the light path during the entire run. At this wavelength no photocatalytic effect was found. In the copper system, with an excess of ytterbium as exchanging metal ion, no photocatalytic effect could be observed either. These runs were therefore carried out directly in the cuvette.

The rate law has been deduced by assuming a steady state concentration for the hydrogen ions. The validity of this assumption was tested for some of the reactions in the ytterbium system by measuring the emf of the cell given above. By this procedure it was verified that the pH of the solution remained constant during the reaction.

The solutions S and T had the following compositions:



Equal volumes of the solutions S and T were mixed. The reactions were followed during approximately three half-lives. The first reading was taken after about one half of a half-life. The data in Tables 4.1 - 4.3 are averages of three independent measurements.

Calculations and results. The errors in the observed rate constants, evaluated according to eq 2.21, were approximately $\pm 5\%$. The precision of the emf of the cell was about ± 0.1 mV, corresponding to an error of about 1% in the hydrogen ion concentration.

The stability constants used for the lanthanoid EDTA complexes, were those of Betts and Dahlinger⁷. However, these constants are valid

Table 4.1. Rate data for the ytterbium system,

L = Yb and M = Cu

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10^4}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10^4}{s^{-1}}$
$C_L^0 = 2.99 \cdot 10^{-4} M$ $C_A^0 = 2.00 \cdot 10^{-4} M$ $C_M^0 = 4.99 \cdot 10^{-3} M$			
4.27	0.639	- 4.3	0.560
5.76	1.02	- 1.1	0.901
7.23	1.54	6.5	1.38
8.75	1.91	- 1.9	1.73
10.26	2.52	0.6	2.30
11.8	3.49	11.6	3.23
13.3	3.78	- 0.6	3.51
15.0	4.60	- 1.1	4.32
16.3	5.56	4.1	5.27
19.2	7.07	0.8	6.80
22.2	8.97	0.4	8.77
25.1	10.7	- 3.3	10.6
28.3	13.4	- 0.4	13.6
31.4	15.7	- 2.1	16.1
$C_L^0 = 2.99 \cdot 10^{-4} M$ $C_A^0 = 2.00 \cdot 10^{-4} M$ $C_M^0 = 9.97 \cdot 10^{-3} M$			
9.20	1.84	-6.6	1.78
$C_L^0 = 4.55 \cdot 10^{-4} M$ $C_A^0 = 4.00 \cdot 10^{-4} M$ $C_M^0 = 9.97 \cdot 10^{-3} M$			
2.04	0.243	- 0.1	0.214
18.1	6.17	- 1.5	5.98
30.2	15.4	3.7	15.9

Table 4.1. Rate data for the ytterbium system,
continued

L = Yb and M = Cu

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10^4}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10^4}{s^{-1}}$
$C_L^0 = 7.00 \cdot 10^{-4} M$ $C_A^0 = 2.00 \cdot 10^{-4} M$ $C_M^0 = 9.97 \cdot 10^{-3} M$			
6.15	1.07	- 4.2	0.965
18.5	6.24	- 3.8	6.09
26.8	12.5	3.3	12.8
$C_L^0 = 2.99 \cdot 10^{-4} M$ $C_A^0 = 2.00 \cdot 10^{-4} M$ $C_M^0 = 1.50 \cdot 10^{-2} M$			
11.1	2.79	8.1	2.80
$C_L^0 = 4.00 \cdot 10^{-4} M$ $C_A^0 = 3.00 \cdot 10^{-4} M$ $C_M^0 = 1.50 \cdot 10^{-2} M$			
2.01	0.231	2.1	0.215
14.3	3.85	- 4.3	3.86
22.6	8.09	- 6.1	8.44
30.8	14.7	0.2	15.9
$C_L^0 = 2.99 \cdot 10^{-4} M$ $C_A^0 = 2.00 \cdot 10^{-4} M$ $C_M^0 = 1.99 \cdot 10^{-2} M$			
11.2	2.73	5.4	2.78
20.0	7.58	10.6	8.05
26.5	11.0	0.1	12.1
30.2	13.2	- 4.5	14.7

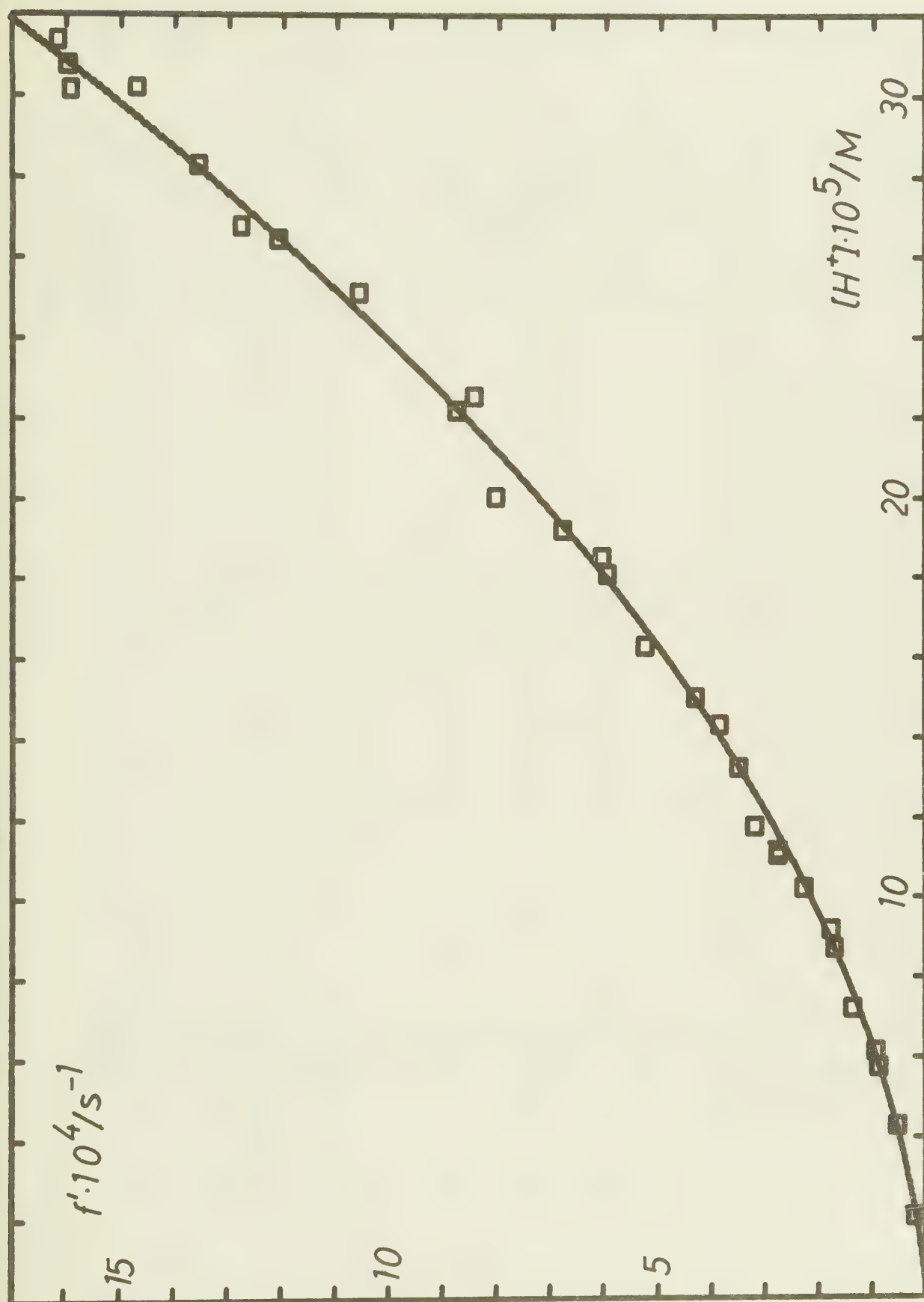


Fig. 4.1 f' as a function of the hydrogen ion concentration for the ytterbium system.

Table 4.2. Rate data for the erbium system,

L = Er and M = Cu

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10^3}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10^3}{s^{-1}}$
$C_L^0 = 2.00 \cdot 10^{-4} M$ $C_A^0 = 1.94 \cdot 10^{-4} M$ $C_M^0 = 4.99 \cdot 10^{-3} M$			
1.21	0.126	4.5	0.124
1.67	0.160	- 7.2	0.157
2.45	0.268	1.1	0.267
3.16	0.368	3.0	0.369
4.68	0.560	- 3.0	0.568
6.17	0.777	- 5.5	0.796
7.67	1.17	6.9	1.22
9.22	1.45	2.5	1.52
10.7	1.72	- 0.9	1.82
12.2	2.10	0.6	2.25
14.0	2.52	- 1.5	2.72
15.1	2.92	2.1	3.18
16.4	3.20	- 0.8	3.52
18.0	3.65	- 1.9	4.05
$C_L^0 = 3.19 \cdot 10^{-4} M$ $C_A^0 = 3.12 \cdot 10^{-4} M$ $C_M^0 = 4.99 \cdot 10^{-3} M$			
5.44	0.682	- 3.2	0.689
6.51	0.893	0.7	0.913
9.55	1.50	1.0	1.57

Table 4.2. Rate data for the erbium system,
continued

L = Er and M = Cu

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10^3}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10^3}{s^{-1}}$
$C_L^0 = 7.02 \cdot 10^{-4} M$ $C_A^0 = 3.12 \cdot 10^{-4} M$ $C_M^0 = 4.99 \cdot 10^{-3} M$			
2.03	0.208	- 4.6	0.202
6.12	0.831	2.7	0.859
10.2	1.54	- 3.9	1.64
14.3	2.45	- 5.1	2.70
18.5	4.05	7.5	4.66
$C_L^0 = 2.00 \cdot 10^{-4} M$ $C_A^0 = 1.94 \cdot 10^{-4} M$ $C_M^0 = 7.48 \cdot 10^{-3} M$			
3.38	0.420	9.0	0.425
7.04	0.988	1.6	1.03
8.22	1.16	- 3.3	1.21
11.4	1.90	- 0.1	2.03
13.2	2.33	0.1	2.52
16.6	3.32	0.9	3.66
$C_L^0 = 2.00 \cdot 10^{-4} M$ $C_A^0 = 1.94 \cdot 10^{-4} M$ $C_M^0 = 9.97 \cdot 10^{-3} M$			
2.80	0.322	4.8	0.325
4.00	0.472	0.1	0.480

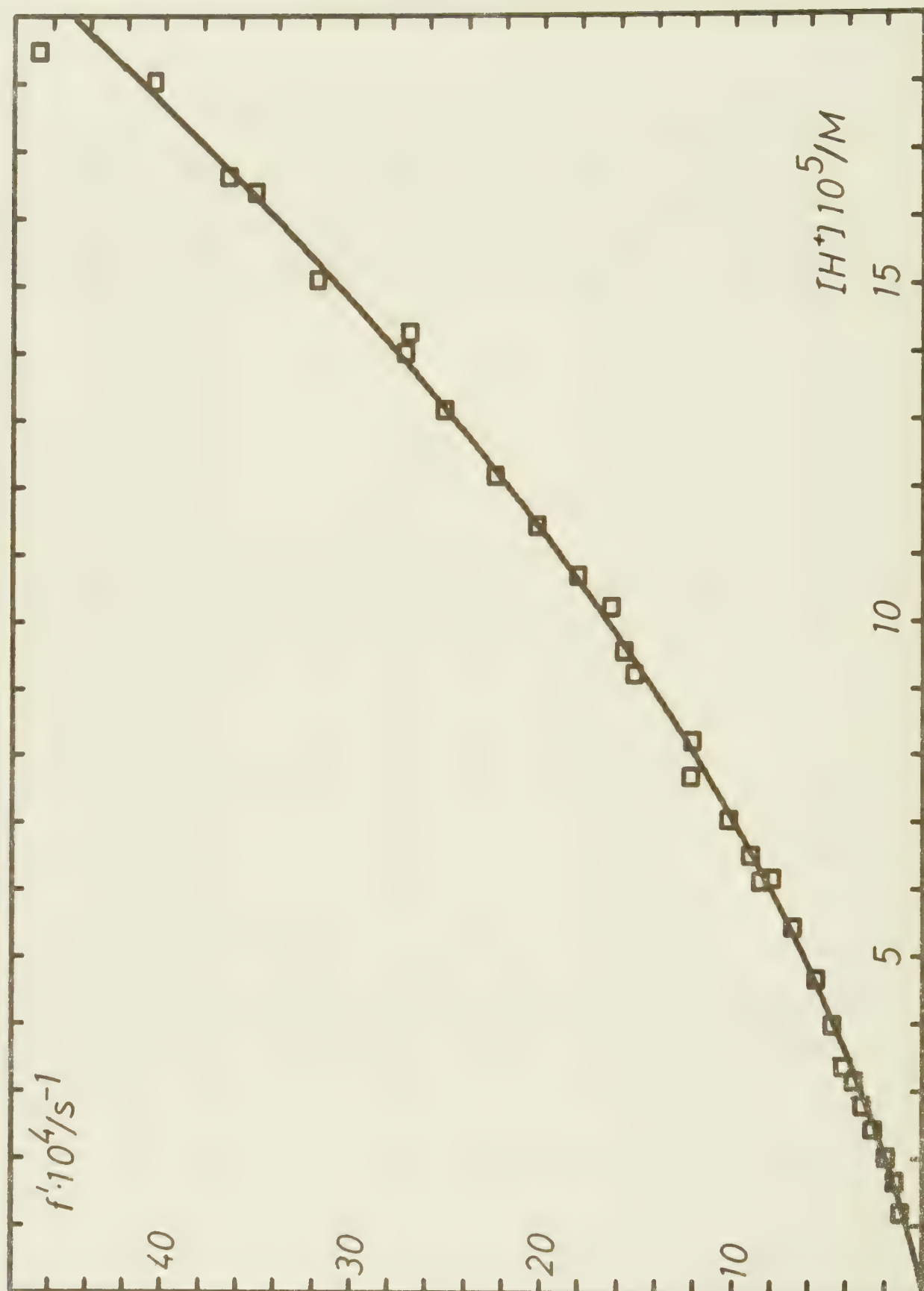


Table 4.3. Rate data for the copper system,

L = Cu and M = Yb

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10^3}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10^3}{s^{-1}}$
$C_L^0 = 4.36 \cdot 10^{-4} M$ $C_A^0 = 2.02 \cdot 10^{-4} M$ $C_M^0 = 5.03 \cdot 10^{-3} M$			
7.05	0.558	- 1.8	0.702
17.1	1.69	- 1.4	2.18
27.2	3.20	- 0.5	4.38
37.2	4.64	- 7.3	6.70
$C_L^0 = 5.98 \cdot 10^{-4} M$ $C_A^0 = 1.00 \cdot 10^{-4} M$ $C_M^0 = 7.47 \cdot 10^{-3} M$			
5.55	0.432	- 0.7	0.551
17.0	1.73	3.0	2.26
33.8	4.60	6.4	6.69
44.9	6.46	0.0	9.99
56.0	9.23	4.7	15.4

Table 4.3. Rate data for the copper system,
continued

L = Cu and M = Yb

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10^3}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10^5}{s^{-1}}$
$C_L^0 = 5.98 \cdot 10^{-4} M$ $C_A^0 = 1.00 \cdot 10^{-4} M$ $C_M^0 = 1.01 \cdot 10^{-2} M$			
2.51	0.216	1.9	0.281
5.46	0.437	- 2.2	0.532
8.73	0.738	- 2.2	0.896
11.6	1.09	2.7	1.35
14.9	1.53	5.2	1.93
17.6	1.85	2.3	2.36
21.1	2.24	- 2.9	2.90
24.1	2.60	- 5.7	3.43
29.2	3.61	0.2	4.96
35.4	4.62	- 1.7	6.59
41.8	5.70	- 4.1	8.47
47.2	6.87	- 2.3	10.6
52.8	8.05	- 2.3	12.9
58.7	9.93	4.0	16.5
64.4	10.9	0.2	18.7
$C_L^0 = 8.02 \cdot 10^{-4} M$ $C_A^0 = 3.29 \cdot 10^{-4} M$ $C_M^0 = 1.27 \cdot 10^{-2} M$			
7.03	0.585	- 0.7	0.711
12.0	1.11	- 0.5	1.37
22.1	2.55	3.6	3.34
32.1	3.93	- 4.6	5.44

Table 4.3. Rate data for the copper system,
continued

L = Cu and M = Yb

$\frac{[\text{H}^+] \cdot 10^5}{\text{M}}$	$\frac{k_{\text{obs}} \cdot 10^3}{\text{s}^{-1}}$	$\frac{k_{\text{obs}} - k_{\text{calc}}}{k_{\text{calc}}} \cdot 100$	$\frac{f'_{\text{exp}} \cdot 10^3}{\text{s}^{-1}}$
$C_{\text{L}}^0 = 2.00 \cdot 10^{-3} \text{ M} \quad C_{\text{A}}^0 = 2.02 \cdot 10^{-4} \text{ M} \quad C_{\text{M}}^0 = 1.27 \cdot 10^{-2} \text{ M}$			
7.24	0.513	- 0.2	0.739
17.6	1.69	4.6	2.44
27.9	3.26	6.0	4.96
38.2	5.09	5.5	8.17

Fig. 4.3 f' as a function of the hydrogen ion concentration for the copper system

at 25 °C and at an ionic strength of 0.1 M, using potassium chloride as neutral salt. The stability constant for the copper EDTA complex has been determined by Schwarzenbach et al.³ at 20 °C and in a 0.1 M potassium chloride medium. The corresponding constant at 25 °C was calculated by using the enthalpy value, given by Case and Stavely²⁶. However, all measurements in the present work were carried out at the ionic strength 0.5 M. The 0.1 M medium constants were used in the calculations, since in most cases the rate constants are rather insensitive to changes of the equilibrium constants.

The constants for formation of the acid complexes were those of Kolat and Powell²⁴ for the lanthanoids, and of Schwarzenbach³ for copper. The following constants were used in the calculations:

	$\log \beta_{LA}$	$\log K_{LAH}$
Cu	18.68	3.0
Er	18.37	2.8
Yb	18.99	2.7

The calculations were performed by a digital computer, using a program written by Ekström and Ryhl. Details of the procedure are given in the appendix. The constants of the erbium system were controlled by graphical methods. In none of the above systems could a direct reaction (path II) be detected, i.e. $f^D = 0$ within the experimental errors. The function f' for the lanthanoid and copper systems is

$$f' = \bar{k}_1 [H^+] + \bar{k}_2 [H^+]^2$$

and

$$f' = k_0 + \bar{k}_1 [H^+] + \bar{k}_2 [H^+]^2, \text{ respectively.}$$

Here, $\bar{k}_1 = K_{LAH} \cdot k_1$ and $\bar{k}_2 = K_{LAH_2} \cdot k_2$.

The dominating term in the available range of concentration is in both cases $\bar{k}_1[H^+]$, corresponding to the dissociation of the monoprotonated complex.

The rate constants, together with their confidence limits on the 99% level of significance, are given in Table 4.4.

Table 4.4

	k_o/s^{-1}	$\bar{k}_1/s^{-1}M^{-1}$	$\bar{k}_2/s^{-1}M^{-2}$
Yb	-	0.76 ± 0.08	$(1.43 \pm 0.07) 10^4$
ref 10	-	0.70	$2.33 \cdot 10^4$
Er	-	8.9 ± 0.5	$(7.7 \pm 0.7) 10^4$
Cu	$(9.0 \pm 5.1) 10^5$	6.5 ± 1.0	$(3.5 \pm 0.3) 10^4$

The agreement with the constants of Betts et al.¹⁰ for the ytterbium system is very good for $\bar{k}_1$ and acceptable for $\bar{k}_2$. Even if the values of β_{LAH} were changed by 20%, the rate constants remain within the given errors. In order to calculate the rate constants k_1 and k_2 , the values of K_{LAH} and K_{LAH_2} must be known. K_{LAH} has been reported²⁴ with rather high accuracy, whereas for some lanthanoids K_{LAH_2} values have only been estimated from kinetic measurements¹⁷.

Chapter 5

POLAROGRAPHIC MEASUREMENTS

The europium EDTA system was studied by using ytterbium as the exchanging metal ion in order to investigate if the over-all reaction proceeds to a measurable extent over the direct substitution (path II) when both metals are lanthanoids. For reasons mentioned earlier, the reaction is difficult to follow by spectrophotometric measurements.

The polarographic half-wave potentials of the free europium ion and its EDTA complex are well separated from one another and from those of the other lanthanoid ions ²⁷. Hence, it is possible to follow the exchange reaction by measuring the diffusion current of the free europium ion when the reaction rate is suitable.

Fig 5.1 shows the waves of three different solutions, recorded by a Radiometer PO 4 polarograph with a dropping mercury electrode (dropping time 2.7 s and flow rate 3.37 mg/s) against a saturated calomel electrode, S.C.E., as a reference. The three solutions were of the following compositions: i) 5.89 mM Eu^{3+} ii) 5.89 mM Eu^{3+} and 2.9 mM EDTA and iii) 5.89 mM Eu^{3+} and ~ 10 mM EDTA. The pH of the solutions was adjusted to about 4 by an acetate buffer ($C_{\text{NaAc}} = 12.5$ mM). Potassium chloride was added to an ionic strength of 0.5 M. The solutions also contained 0.01% gelatin to suppress polarographic maxima. The half-wave potential vs. S.C.E. was found to be -0.72 V for europium chloride and -1.03 V for europium EDTA.

The polarograph was equipped with a fast recorder, type Servogor RE 511, in order to record concentration vs. time curves. The concentration of uncomplexed europium was followed at a constant voltage of -0.85 V.



Fig. 5.1. Polarographic waves for europium chloride and europium EDTA complex. The solutions were
 1) 5.89 mM Eu^{3+} , 2) 5.89 mM Eu^{3+} and 2.9 mM EDTA and
 3) 5.89 mM Eu^{3+} and 10 mM EDTA.
 Medium pH = 4, $[\text{NaAc}] = 12.5 \text{ mM}$, $I = 0.5 \text{ M (KCl)}$,
 and 0.01% gelatin.

The solutions had the following compositions:

$$\begin{array}{ll}
 \text{S: } \left\{ \begin{array}{l} 6.67 \text{ } C_M^{\circ} \\ 6.67 \text{ } C_A^{\circ} \\ I = 0.5 \text{ M (KCl)} \end{array} \right. & \text{T: } \left\{ \begin{array}{l} 1.18 \text{ } C_M^{\circ} \\ 1.18 \cdot 12.5 \text{ mM NaAc} \\ \text{var. HAc} \\ 1.18 \cdot 0.01\% \text{ gelatin} \\ I = 0.5 \text{ M (KCl)} \end{array} \right.
 \end{array}$$

3.00 ml of the thermostated solution T was injected by a syringe into 17.0 ml of solution S, which was thermostated in the reaction vessel. The mixing time was less than 3 s. The reaction was followed during at least three half-lives. Before mixing, dissolved oxygen was removed by bubbling nitrogen through the solutions.

It was not possible to vary the hydrogen ion concentration more than by a factor of 5, because precipitation of hydroxo complexes occurred at low hydrogen ion concentrations, and in more acid solutions the reaction rates became too fast for the experimental method. This can be used only for reactions with half-lives longer than 15 s²⁸. From some preliminary experiments it was found that a moderate change in the gelatin concentration did not affect the observed rate constants. All experimental data are given in Table 5.1 and Fig. 5.2. The given k_{obs} values are averages of at least three independent measurements.

Calculations and results. The observed rate constants were evaluated according to eq (2.21) and were accurate to about $\pm 8\%$. The hydrogen ion concentration was determined with an error of approximately 1%. The following stability constants were used in the calculations:

$\log \beta_{\text{EuA}} = 16.66$,¹ $\log K_{\text{EuAH}} = 2.6$,²⁴ $\log \beta_{\text{YbA}} = 18.99$,¹ and $\log K_{\text{YbAH}} = 2.7$ ²⁴. The calculations were performed by a digital computer, using the program given in the appendix.

Table 5.1. Rate data for the europium system,

L = Eu and M = Yb

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10^2}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10^2}{s^{-1}}$
$C_L^0 = 4.56 \cdot 10^{-4} M \quad C_A^0 = 2.00 \cdot 10^{-4} M \quad C_M^0 = 5.02 \cdot 10^{-3} M$			
1.88	0.701	- 6.3	0.842
3.59	1.49	- 6.2	1.77
5.30	2.24	-12.9	2.62
7.01	3.65	- 1.4	4.33
$C_L^0 = 2.94 \cdot 10^{-4} M \quad C_A^0 = 2.00 \cdot 10^{-4} M \quad C_M^0 = 7.47 \cdot 10^{-3} M$			
2.74	1.28	3.9	1.46
5.73	3.32	6.9	3.65
7.81	4.86	5.1	5.36
$C_L^0 = 2.94 \cdot 10^{-4} M \quad C_A^0 = 2.00 \cdot 10^{-4} M \quad C_M^0 = 1.01 \cdot 10^{-2} M$			
2.38	1.25	12.6	1.35
3.08	1.59	6.6	1.71
3.38	1.84	11.0	1.99
4.36	2.21	- 1.8	2.37
4.99	2.75	3.5	2.96
5.37	3.32	13.8	3.59
5.83	3.21	- 0.6	3.45
6.51	3.64	- 2.0	3.92
7.24	4.28	0.5	4.62
8.59	5.21	- 2.4	5.63

Table 5.1. Rate data for the europium system,
continued

L = Eu and M = Yb

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10^2}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10^2}{s^{-1}}$
$C_L^0 = 2.94 \cdot 10^{-4} M$ $C_A^0 = 1.02 \cdot 10^{-4} M$ $C_M^0 = 1.01 \cdot 10^{-2} M$			
1.82	0.801	- 2.6	0.858
3.42	1.52	- 9.9	1.62
5.02	2.61	- 2.7	2.80
6.62	3.80	0.1	4.09

Fig. 5.2. f' as a function of the hydrogen ion concentration for the europium system.



Analogous to the previously investigated systems, no reaction along path II was found, i.e. $f^D = 0$ within the experimental errors (p.27.). The resulting f' relation for the europium system was found to be

$$f' = \bar{k}_1[H^+] + \bar{k}_2[H^+]^2,$$

where $\bar{k}_1 = K_{EuAH} \cdot k_1$ and $\bar{k}_2 = K_{EuAH_2} \cdot k_2$. The dominating term is $\bar{k}_1[H^+]$, within the concentration range investigated, corresponding to the dissociation of the monoprotonated complex. The following rate constants were obtained:

$$\bar{k}_1 = (4.3 \pm 0.7)10^2 \text{ s}^{-1} \text{ M}^{-1} \text{ and } \bar{k}_2 = (2.8 \pm 1.5)10^6 \text{ s}^{-1} \text{ M}^{-2}.$$

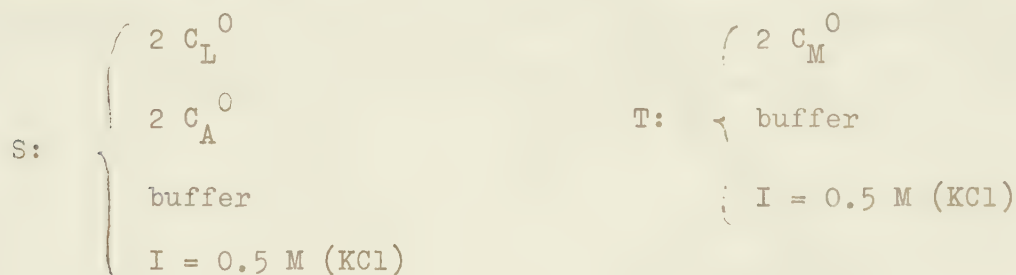
The errors are the confidence limits on the 99% level of significance. The error of $\bar{k}_2$ is rather large, because of the narrow range of hydrogen ion concentrations used. Division of the constant given by D'Olie-slagen and Choppin¹⁸ by β_{Eu}/β_{La} gives $\bar{k}_1 = 6 \cdot 10^2 \text{ s}^{-1} \text{ M}^{-1}$, which is in agreement with the value obtained in the present study.

Chapter 6

STOPPED-FLOW MEASUREMENTS

The substitution rates for the members in the beginning of the lanthanoid series are much faster than for those at the end. Exchange reactions of the neodymium, praseodymium, lanthanum, and copper systems, with half-lives down to a few ms, were therefore studied by a Durrum-Gibson stopped-flow spectrophotometer. The wavelength range used was 600-820 nm. To check that no photochemical effects were present, some solutions were studied at different wavelengths and slitwidths. No differences in the observed rate constants could be detected.

The solutions S and T, which were mixed in equal volumes, had the following compositions:



To remove dissolved air, the solutions were boiled for two minutes at decreased pressure at room temperature. In the lanthanoid systems an excess of copper was used as the exchanging metal ion, whereas in the copper system lanthanum ions were used.

The copper system. The dissociation rates of the copper system, when ytterbium was used as ligand acceptor have been described in chapter 4. In that case, the terms δ_1 and δ_2 in the rate equations might be regarded more or less as correction terms. In order to check the kinetic model for large values of δ_1 and δ_2 , the copper system was also investigated with a large excess of lanthanum ions as ligand acceptor. Then the copper system becomes rate determining, since its

concentration is low compared to the concentration of both complexed and uncomplexed lanthanum.

The rate determining step along path I is then the dissociation of the copper EDTA complexes. From a plot of the observed rate constants vs. the hydrogen ion concentration (Fig. 6.1), it is seen that a separate curve is obtained for each lanthanum ion concentration at a constant concentration of lanthanum complex. At a given pH, the rate decreases for increasing lanthanum ion concentration. This behaviour is exactly what is expected from the kinetic model for large δ -values.

Dependence of the buffer. The effect of the acetate concentration on the rate was investigated in the copper system. Some solutions with varying concentration of acetate at constant hydrogen ion concentration were measured. A moderate increase of the observed rate constant with increasing acetate ion concentration was found (Fig. 6.2). This result is consistent with that of Glentworth et al.¹⁶ for the cerium system.

The experimental data for the neodymium, praseodymium, lanthanum, and copper systems are given in Tables 6.1 - 6.4 and Fig. 6.3 - 6.6.

Calculations and results. The observed rate constants were accurate to about $\pm 5\%$. The hydrogen ion concentration was determined with an error of approximately 1%.

The stability constants used are given in Table 6.5.

Table 6.5 Stability constants used in the calculations.

System	$\log \beta_{LA}$	Ref.	$\log K_{LAH}$	Ref.
Cu	18.68	3	3.0	3
Nd	16.05	1	2.5	24
Pr	15.76	1	2.5	24
La	15.19	1	2.4	24

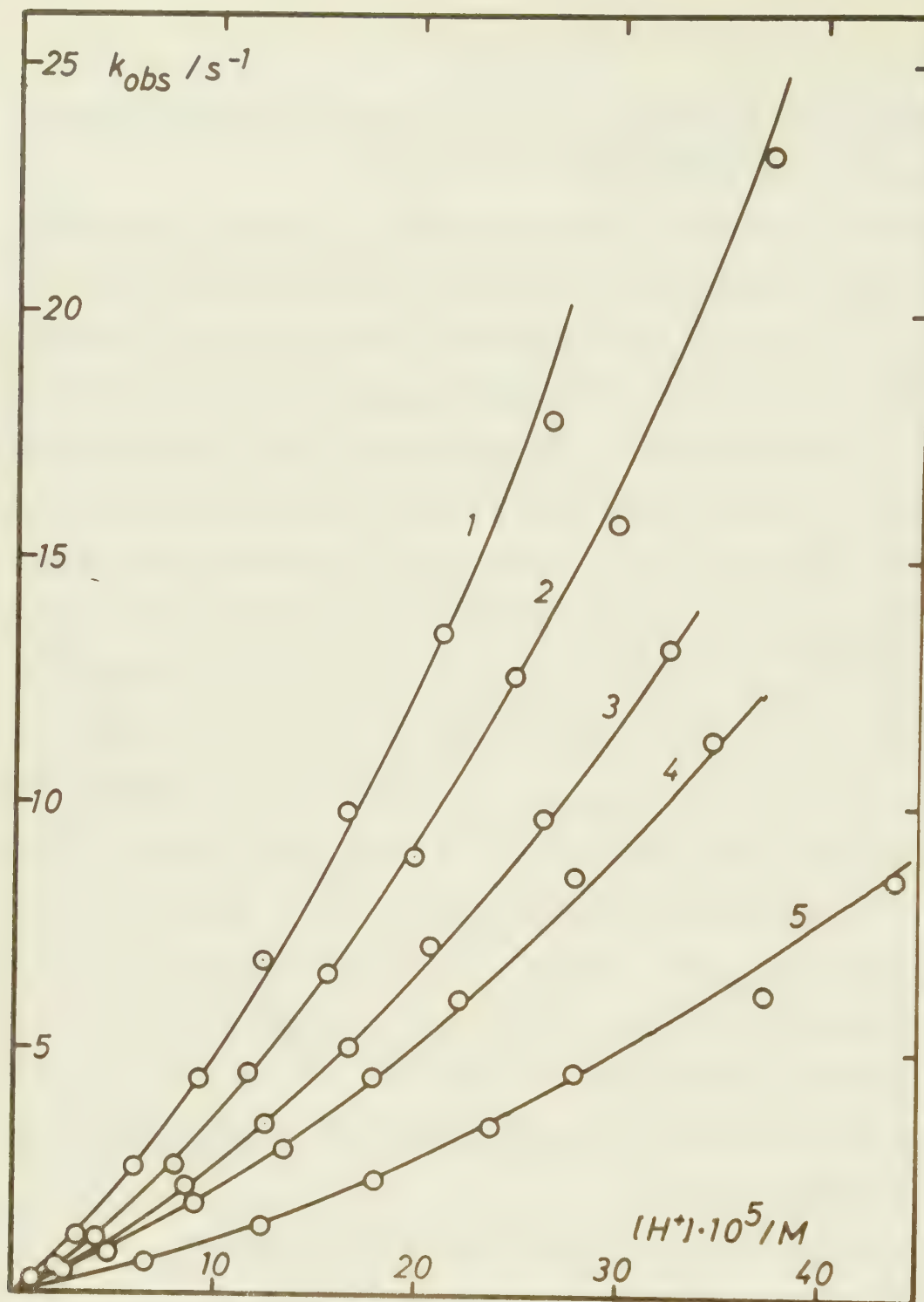


Fig. 6.1. The observed rate constant, k_{obs} , for the copper system as a function of the hydrogen ion concentration. In all cases $C_{\text{Cu}}^0 = 2.00 \cdot 10^{-4} \text{ M}$ and $C_{\text{A}}^0 = 5.00 \cdot 10^{-3} \text{ M}$. The concentration of lanthanum ions, C_{LA}^0 , is 1) $8.58 \cdot 10^{-3} \text{ M}$, 2) $1.00 \cdot 10^{-2} \text{ M}$, 3) $1.24 \cdot 10^{-2} \text{ M}$, 4) $1.50 \cdot 10^{-2} \text{ M}$, and 5) $2.50 \cdot 10^{-2} \text{ M}$.

The full-drawn curves have been calculated from the obtained rate constants of f' and f^D . Some of the experimental points close to the origin have been omitted for clarity.

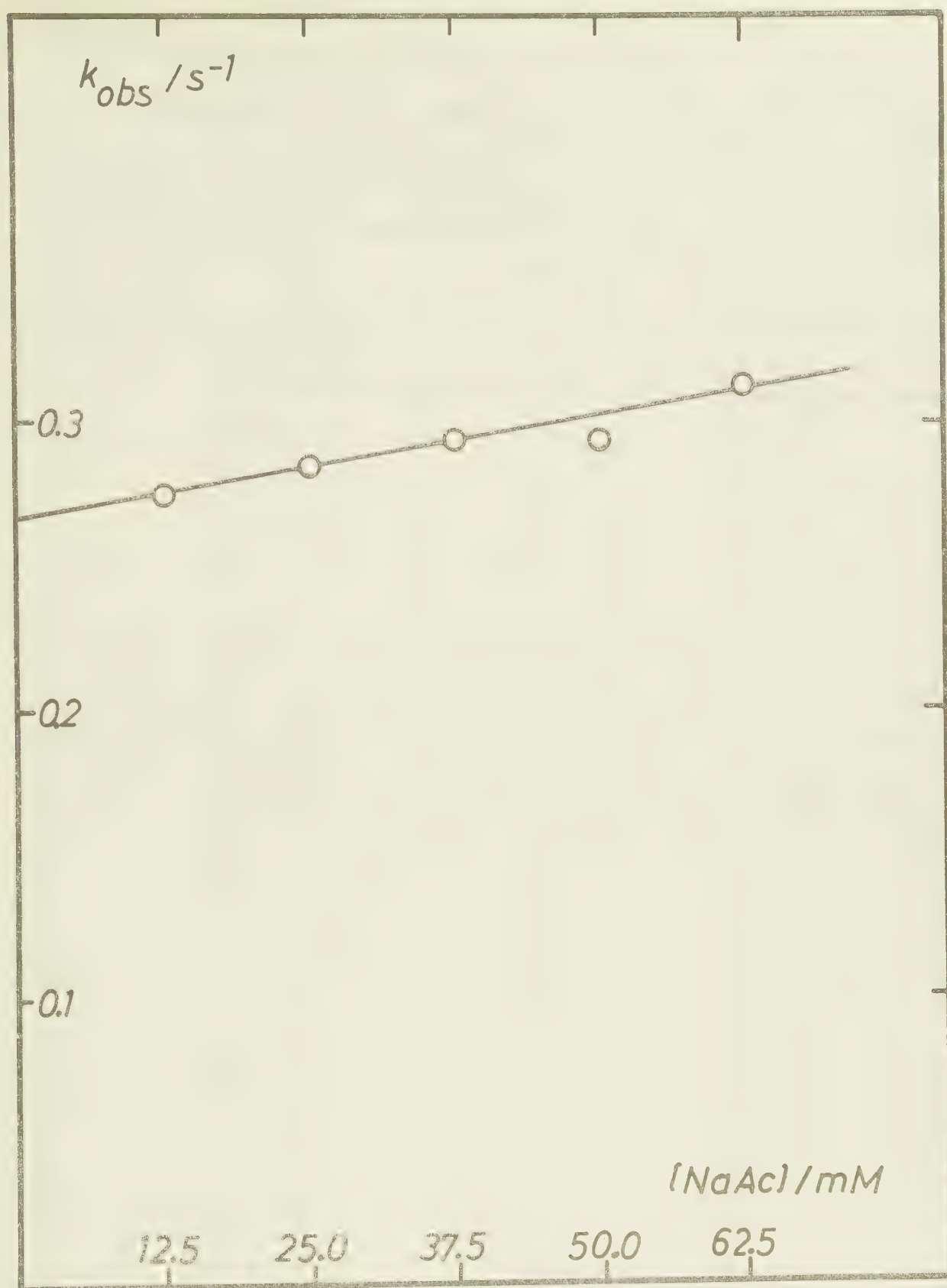


Fig 6.2. The observed rate constant, k_{obs} , for the copper system as a function of the acetate concentration. $[H^+] = 0.85 \cdot 10^{-5}$ M, $C_{Cu}^0 = 2.00 \cdot 10^{-4}$ M, $C_A^0 = 5.00 \cdot 10^{-3}$ M, and $C_{La}^0 = 8.58 \cdot 10^{-3}$ M.

Table 6.1. Rate data for the neodymium system

L = Nd and M = Cu

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10}{s^{-1}}$
$C_L^0 = 6.78 \cdot 10^{-4} M \quad C_A^0 = 6.40 \cdot 10^{-4} M \quad C_M^0 = 4.99 \cdot 10^{-3} M$			
22.4	2.77	9.8	3.07
$C_L^0 = 6.78 \cdot 10^{-4} M \quad C_A^0 = 6.40 \cdot 10^{-4} M \quad C_M^0 = 9.98 \cdot 10^{-3} M$			
4.11	0.445	- 0.1	0.459
7.57	0.862	3.9	0.865
20.5	2.40	2.5	2.59
34.7	4.58	11.3	5.45
41.6	5.07	1.1	5.80
57.4	7.22	0.6	8.61
$C_L^0 = 3.39 \cdot 10^{-4} M \quad C_A^0 = 3.20 \cdot 10^{-4} M \quad C_M^0 = 1.50 \cdot 10^{-2} M$			
4.90	0.539	0.1	0.551
9.06	0.983	- 2.0	1.02
12.1	1.31	- 3.6	1.37
13.4	1.51	0.2	1.59
15.5	1.73	- 1.2	1.83
18.0	2.06	0.3	2.20
21.0	2.36	- 2.6	2.53
25.2	2.86	- 2.4	3.11
27.9	3.24	- 1.2	3.54
33.0	3.87	- 1.1	4.31
38.0	4.58	- 0.1	5.15
43.6	5.26	- 1.2	6.01
48.3	5.83	- 1.9	6.76
54.3	6.60	- 2.7	7.76
60.8	7.88	2.7	9.45

Table 6.1. Rate data for the neodymium system
continued

L = Nd and M = Cu

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10}{s^{-1}}$
$C_L^0 = 6.78 \cdot 10^{-4} M$ $C_A^0 = 3.20 \cdot 10^{-4} M$ $C_M^0 = 1.50 \cdot 10^{-2} M$			
3.78	0.423	2.6	0.433
11.9	1.30	- 2.5	1.36
20.0	2.25	- 1.5	2.42
24.0	2.89	3.7	3.14
32.1	3.74	- 1.7	4.15
36.2	4.30	- 0.7	4.83
$C_L^0 = 6.78 \cdot 10^{-4} M$ $C_A^0 = 6.40 \cdot 10^{-4} M$ $C_M^0 = 2.00 \cdot 10^{-2} M$			
27.7	3.08	- 5.1	3.37
30.5	3.59	- 0.4	3.96

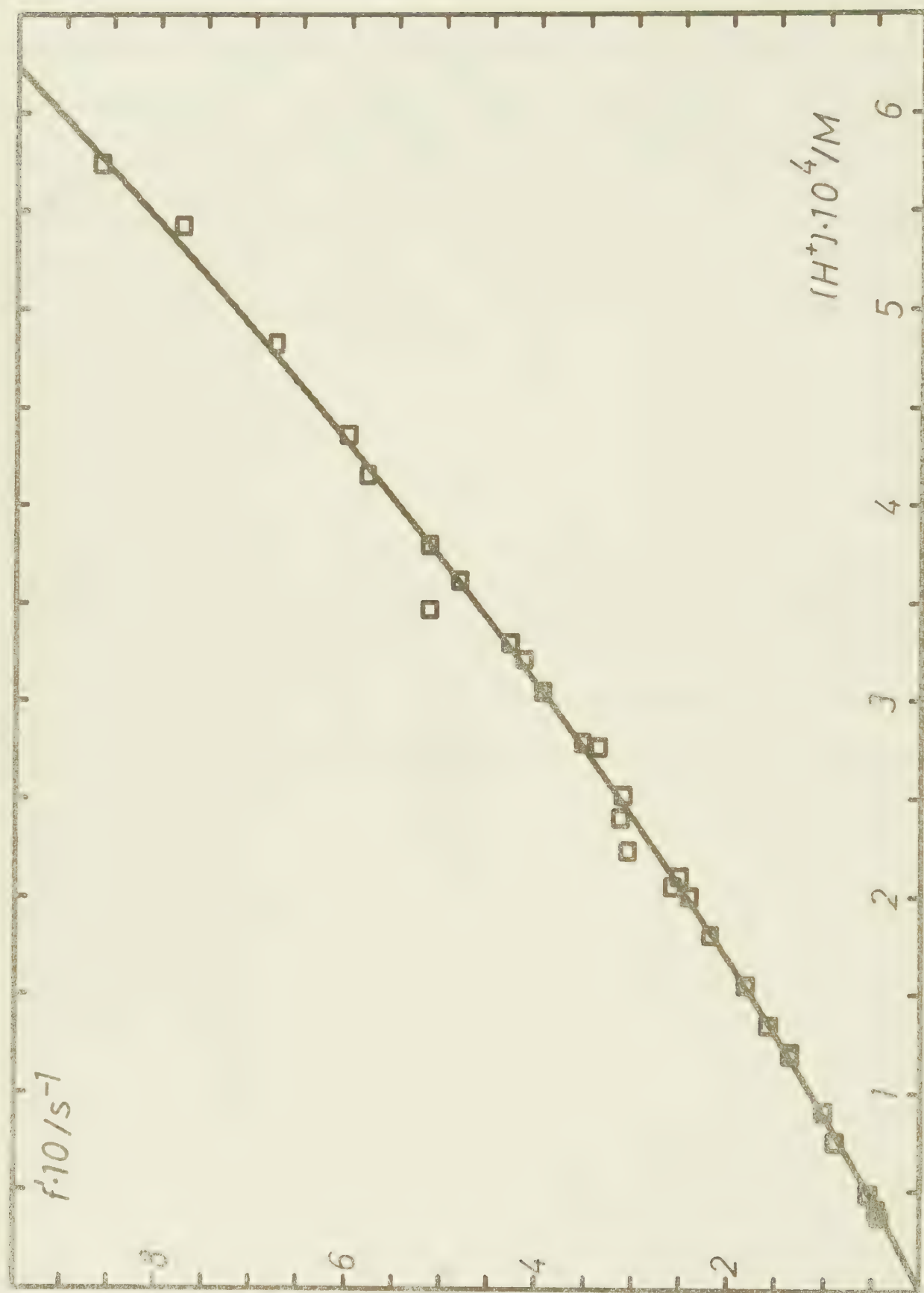
Fig. 6.3. f' as a function of the hydrogen ion concentration for the neodymium system.

Table 6.2. Rate data for the praseodymium system

L = Pr and M = Cu

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10}{s^{-1}}$
$C_L^0 = 6.20 \cdot 10^{-4} M$ $C_A^0 = 6.00 \cdot 10^{-4} M$ $C_M^0 = 1.50 \cdot 10^{-3} M$			
9.00	1.43	5.5	1.68
12.9	2.11	8.6	2.49
24.6	4.12	7.0	4.89
32.8	5.54	5.0	6.64
$C_L^0 = 3.10 \cdot 10^{-4} M$ $C_A^0 = 3.00 \cdot 10^{-4} M$ $C_M^0 = 4.99 \cdot 10^{-3} M$			
6.60	1.08	- 4.3	1.12
21.2	3.73	3.8	4.01
$C_L^0 = 3.10 \cdot 10^{-4} M$ $C_A^0 = 3.00 \cdot 10^{-4} M$ $C_M^0 = 9.98 \cdot 10^{-3} M$			
3.21	0.616	4.0	0.626
4.34	0.759	- 1.8	0.774
16.5	2.88	3.2	3.04
20.0	3.51	3.2	3.74
29.6	5.03	- 1.8	5.50
40.1	7.61	7.4	8.56

Table 6.2. Rate data for the praseodymium system
continued

L = Pr and M = Cu

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10}{s^{-1}}$
$C_L^0 = 3.10 \cdot 10^{-4} M$ $C_A^0 = 5.00 \cdot 10^{-4} M$ $C_M^0 = 1.50 \cdot 10^{-2} M$			
4.81	0.850	0.0	0.866
8.09	1.52	- 4.5	1.36
11.9	1.98	- 2.0	2.06
14.6	2.41	- 2.2	2.52
17.9	2.96	- 2.5	3.13
20.2	3.56	3.3	3.79
23.7	4.18	2.9	4.49
27.4	4.63	- 1.9	5.02
31.5	5.38	- 1.7	5.90
37.5	6.45	2.3	7.19
46.1	8.23	- 0.4	9.39
53.7	9.66	- 1.1	11.2
60.7	10.9	- 2.6	12.9
$C_L^0 = 3.10 \cdot 10^{-4} M$ $C_A^0 = 3.00 \cdot 10^{-4} M$ $C_M^0 = 2.00 \cdot 10^{-2} M$			
10.3	1.62	- 7.5	1.68
26.5	4.47	- 2.1	4.84
$C_L^0 = 6.20 \cdot 10^{-4} M$ $C_A^0 = 3.00 \cdot 10^{-4} M$ $C_M^0 = 2.00 \cdot 10^{-2} M$			
3.97	0.727	1.8	0.741
11.9	1.98	- 1.2	2.06
19.9	3.40	0.6	3.62
27.9	4.81	0.1	5.23
35.8	5.99	- 4.6	6.66

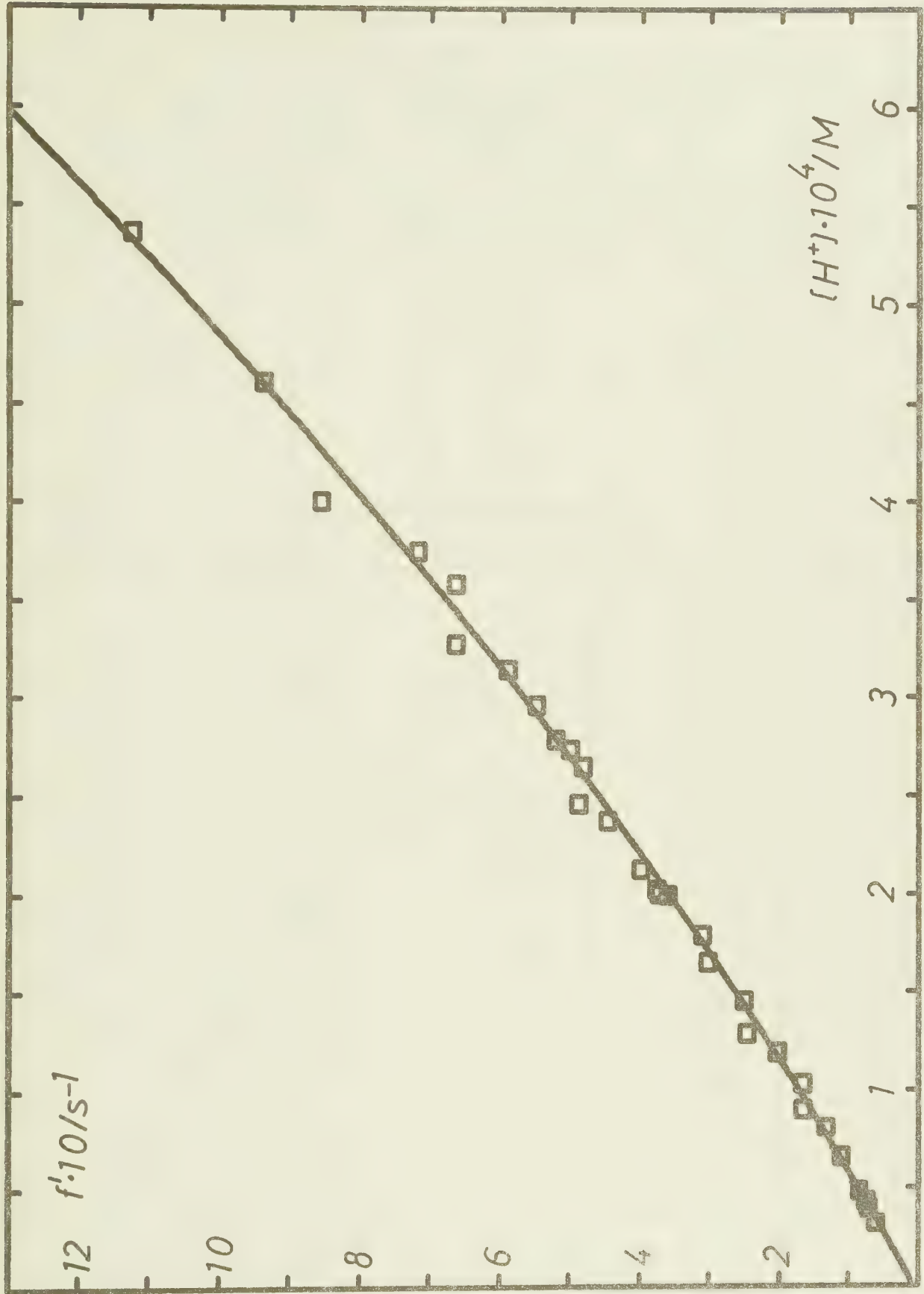


Fig. 6.4. f' as a function of the hydrogen ion concentration for the praseodymium system.

Table 6.3. Rate data for the lanthanum system

L = La and M = Cu

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10}{s^{-1}}$
$C_L^0 = 2.06 \cdot 10^{-4} M$ $C_A^0 = 2.00 \cdot 10^{-4} M$ $C_M^0 = 4.99 \cdot 10^{-3} M$			
1.95	0.925	- 0.9	0.932
3.69	1.64	2.7	1.65
12.0	5.15	5.4	5.24
20.8	9.09	5.4	9.32
33.4	15.2	5.6	15.7
$C_L^0 = 5.26 \cdot 10^{-4} M$ $C_A^0 = 5.00 \cdot 10^{-4} M$ $C_M^0 = 9.98 \cdot 10^{-3} M$			
3.12	1.46	6.0	1.47
3.83	1.70	5.1	1.72
4.54	1.90	- 1.3	1.92
7.41	3.29	7.8	3.30
10.6	4.13	- 4.7	4.19
13.7	5.82	4.1	5.92
17.2	7.07	0.2	7.22
20.5	8.42	- 1.1	8.62
23.9	10.0	0.5	10.5
27.4	11.5	- 2.3	11.7
33.3	14.8	5.4	15.4
41.3	19.4	6.6	20.2
47.3	21.2	- 0.1	22.3
55.0	25.7	1.8	27.2

Table 6.3. Rate data for the lanthanum system
continued

L = La and M = Cu

$\frac{[H^+] \cdot 10^5}{M}$	$\frac{k_{obs} \cdot 10}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10}{s^{-1}}$
$C_L^0 = 3.26 \cdot 10^{-4} M$ $C_A^0 = 3.00 \cdot 10^{-4} M$ $C_M^0 = 1.50 \cdot 10^{-2} M$			
2.80	1.21	- 4.1	1.22
3.61	1.51	- 3.9	1.52
4.12	1.82	2.9	1.83
5.27	2.16	- 2.6	2.18
8.92	3.59	- 1.8	3.64
13.1	5.15	- 4.1	5.23
15.8	6.12	- 5.4	6.23
21.6	8.49	- 5.7	8.69
24.3	9.91	- 2.5	10.2
27.9	11.8	- 0.6	12.1
32.1	13.9	0.9	14.4
38.2	17.0	1.8	17.7
47.2	20.7	- 2.1	21.8
54.4	24.0	- 3.7	25.4
62.0	28.5	- 2.0	30.3

Fig. 6.5. f' as a function of the hydrogen ion concentration for the lanthanum system.



Table 6.4. Rate data for the copper system

L = Cu and M = La

$\frac{[H^+]}{M} \cdot 10^5$	$\frac{k_{obs}}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10^4}{s^{-1}}$	$\frac{f^D_{exp} \cdot 10^3}{s^{-1} M^{-1}}$
$C_L^0 = 2.00 \cdot 10^{-4} M$ $C_A^0 = 5.00 \cdot 10^{-3} M$ $C_M^0 = 8.58 \cdot 10^{-3} M$				
0.830	0.281	- 3.9	0.572	0.683
3.07	1.13	- 4.4	2.32	1.97
5.93	2.57	1.9	5.37	12.4
9.09	4.35	1.7	9.19	19.1
12.3	6.83	8.1	14.6	50.4
16.4	9.88	4.9	21.3	54.2
21.1	13.5	0.2	29.3	36.2
26.5	17.9	- 5.8	39.1	- 23.6
$C_L^0 = 2.00 \cdot 10^{-4} M$ $C_A^0 = 5.00 \cdot 10^{-3} M$ $C_M^0 = 1.00 \cdot 10^{-2} M$				
0.338	0.0892	2.5	0.244	0.678
0.940	0.244	- 1.7	0.667	1.28
2.10	0.559	- 3.4	1.54	2.25
3.98	1.16	- 1.7	3.22	5.30
4.86	1.36	- 8.4	3.76	0.530
7.90	2.58	- 3.0	7.29	8.14
11.7	4.50	2.2	12.9	24.7
15.6	6.57	1.5	19.1	31.1
19.8	8.96	- 1.3	26.3	25.1
24.7	12.7	0.8	37.6	45.9
29.8	15.8	- 5.3	47.2	- 5.28
37.7	23.3	- 2.9	70.7	19.0

Table 6.4. Rate data for the copper system
continued

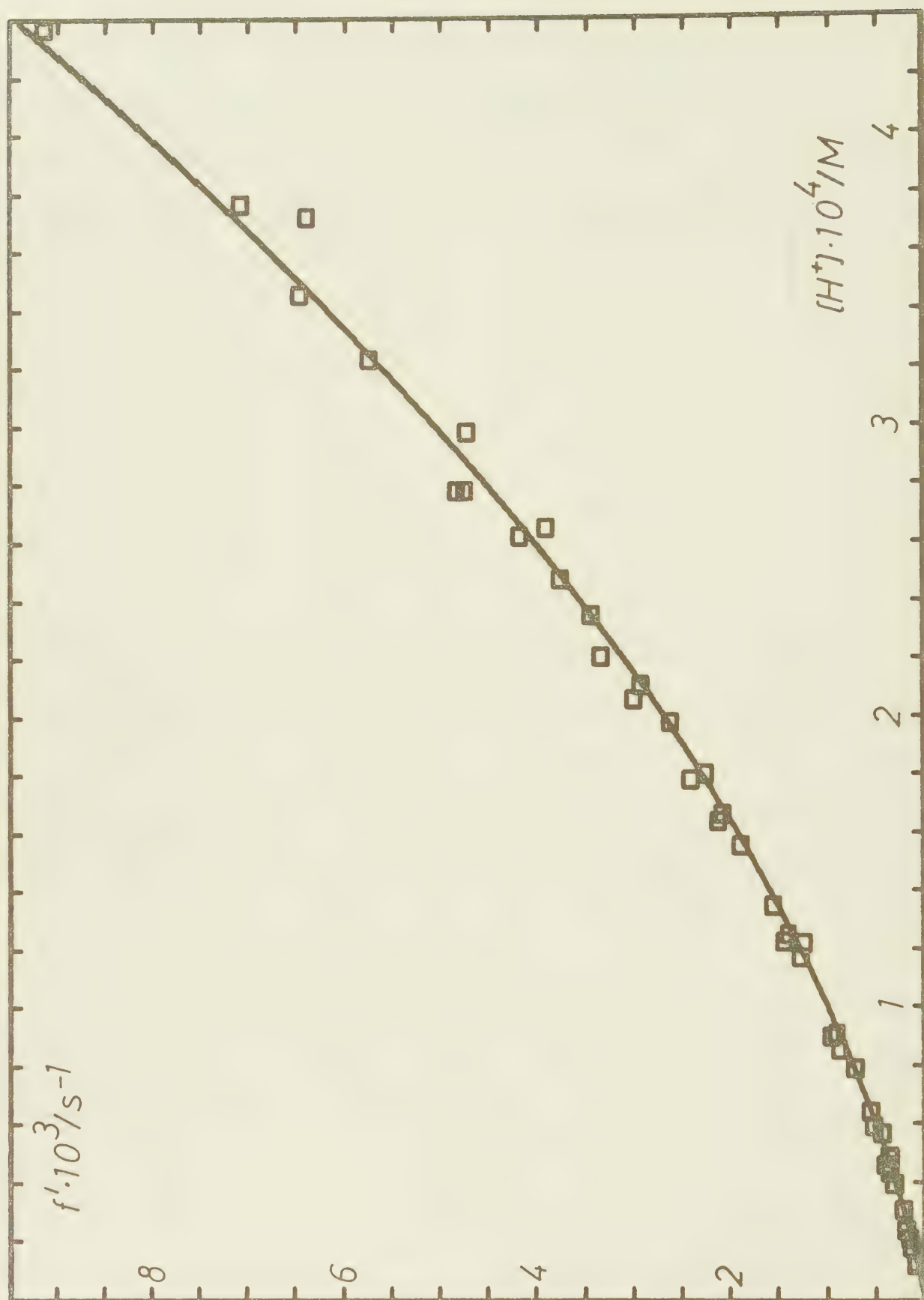
L = Cu and M = La

$\frac{[H^+]}{M} \cdot 10^5$	$\frac{k_{obs}}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10^4}{s^{-1}}$	$\frac{f^D_{exp} \cdot 10^3}{s^{-1} M^{-1}}$
$C_L^0 = 2.00 \cdot 10^{-4} M$ $C_A^0 = 5.00 \cdot 10^{-5} M$ $C_M^0 = 1.24 \cdot 10^{-2} M$				
1.25	0.242	1.0	0.931	2.18
4.37	0.954	2.5	3.76	8.44
8.56	2.20	5.7	8.89	21.0
12.5	3.46	2.1	14.2	24.6
16.7	5.02	0.8	20.8	29.3
20.6	7.13	5.9	30.1	57.3
26.2	9.78	2.1	41.8	54.4
32.4	13.3	0.7	57.4	58.0
$C_L^0 = 2.00 \cdot 10^{-4} M$ $C_A^0 = 5.00 \cdot 10^{-3} M$ $C_M^0 = 1.50 \cdot 10^{-2} M$				
0.531	0.0853	10.1	0.424	1.32
1.220	0.193	5.4	0.953	2.57
2.39	0.396	6.1	1.98	5.22
4.62	0.819	5.6	4.17	10.1
8.99	1.85	7.8	9.70	22.6
13.5	2.97	2.7	15.8	26.5
17.8	4.45	5.1	24.2	41.9
22.1	6.04	5.6	33.4	55.1
27.8	8.59	7.2	48.3	80.2
34.6	11.3	1.8	64.6	68.2

Table 6.4. Rate data for the copper system
continued

L = Cu and M = La

$\frac{[H^+]}{M} \cdot 10^5$	$\frac{k_{obs}}{s^{-1}}$	$\frac{k_{obs} - k_{calc}}{k_{calc}} \cdot 100$	$\frac{f'_{exp} \cdot 10^4}{s^{-1}}$	$\frac{f^D_{exp} \cdot 10^3}{s^{-1} M^{-1}}$
$C_L^0 = 2.00 \cdot 10^{-4} M$ $C_A^0 = 5.00 \cdot 10^{-3} M$ $C_M^0 = 2.50 \cdot 10^{-4} M$				
1.82	0.174	4.9	1.47	3.44
6.46	0.654	- 2.0	5.69	9.71
12.2	1.39	- 4.6	12.6	15.9
18.0	2.37	- 1.9	22.7	26.5
23.5	3.47	- 0.3	34.4	37.5
27.8	4.63	4.9	47.4	58.1
37.2	6.18	- 9.2	63.8	22.3
43.7	8.52	- 1.9	91.2	61.0
$C_L^0 = 2.00 \cdot 10^{-4} M$ $C_A^0 = 5.00 \cdot 10^{-3} M$ $C_M^0 = 1.00 \cdot 10^{-2} M$				
4.86	1.36	- 8.4	3.76	0.530
$C_L^0 = 2.00 \cdot 10^{-4} M$ $C_A^0 = 1.00 \cdot 10^{-2} M$ $C_M^0 = 1.50 \cdot 10^{-2} M$				
4.90	2.70	- 11.6	3.65	- 2.25
$C_L^0 = 2.00 \cdot 10^{-4} M$ $C_A^0 = 1.50 \cdot 10^{-2} M$ $C_M^0 = 2.02 \cdot 10^{-2}$				
5.70	4.74	- 11.2	4.40	- 2.21

Fig. 6.6. f' as a function of the hydrogen ion concentration for the copper system.

The constants in the functions f' and f^D were calculated by a digital computer, using the program given in the appendix. The constants of the lanthanum systems were also checked by graphical methods.

All k_{obs} -values were evaluated according to equation (2.21). In the copper system, a few k_{obs} -values were also calculated from equation (2.20). The differences in k_{obs} -values obtained from the two equations were negligible compared with the experimental errors and the errors of δ_2 . The δ_1 -values are in the range 0.03-0.16, whereas δ_2 varies from $1.6 \cdot 10^3$ to $9.7 \cdot 10^3$. The resulting f' and f^D -values then become inversely proportional to the δ_2 -values, but they are rather insensitive to the δ_1 -values, because δ_1 in equation 2.20 is multiplied with the factor f'/f'' . Since the copper system is much slower than the lanthanum system, it follows that $\delta_1 \cdot f'/f'' \ll 1$.

By minor changes of the stability constants, viz. $\log \beta_{\text{CuA}}$ from 18.68 to 18.71 and $\log \beta_{\text{LaA}}$ from 15.19 to 15.16, a good agreement of the rate constants in path I from the experiments with small and large δ -values, respectively, could be obtained. From the experiment with large δ -values it was not possible to determine the rate constant in path I for the uncatalysed dissociation step, owing to its low value. In this experiment, a hydrogen ion catalysed reaction along path II was also detected. However, the corresponding rate constant is rather inaccurate, because only a small fraction (less than 10%) of the total reaction proceeds along this path.

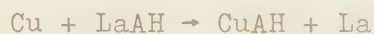
In order to check the error limits of the constants, especially of f^D , the following procedure was used. New values of k_{obs} were produced from the experimental values by means of random normal distributed errors, using $\sigma = 0.05 \cdot k_{\text{obs}}$, which corresponds to the accuracy of the observed rate constants. With these new k_{obs} -values a new set of rate constants were calculated. The results remained within the different confidence limits, determined in the primary calculation, as often as

was statistically expected. Hence, the weighting procedure used seems to have given realistic standard deviations.

The rate of dissociation of the neodymium, praseodymium, lanthanum, and copper EDTA complexes is given by expressions of the type

$$f' = k_0 + \bar{k}_1[H^+] + \bar{k}_2[H^+]^2.$$

For the copper system, a direct substitution reaction, f^D , was found. This corresponds to the reaction



with $f^D = \bar{k}_1^D[H^+]$ and $\bar{k}_1^D = (1.6 \pm 0.5)10^2 \text{ s}^{-1} \text{ M}^{-2}$.

The rate constants of f' are given in Table 6.6, where the errors are the confidence limits at the 99% level of significance.

Table 6.6

	k_0/s^{-1}	$\bar{k}_1/\text{s}^{-1} \text{ M}^{-1}$	$\bar{k}_2/\text{s}^{-1} \text{ M}^{-2}$
Nd	-	$(1.09 \pm 0.04)10^3$	$(7.0 \pm 1.5)10^5$
ref 10	-	$1.08 \cdot 10^3$	-
ref 17	-	$6.6 \cdot 10^2$	-
Pr	$(9.0 \pm 7.5)10^3$	$(1.6 \pm 0.1)10^3$	$(1.0 \pm 0.4)10^6$
ref 11		$1.7 \cdot 10^3$	-
La	$(2.0 \pm 1.0)10^{-2}$	$(5.7 \pm 0.5)10^5$	$(1.9 \pm 0.7)10^6$
ref 10	-	$7.0 \cdot 10^5$	-
Cu	-	6.9 ± 0.3	$(3.3 \pm 0.3)10^4$

The constants are products of rate constants, k_i , and the corresponding constant K_{LAH_i} (eqn 2.3).

Chapter 7

NUCLEAR MAGNETIC RESONANCE MEASUREMENTS

The previously used exchange method is not applicable to alkaline solutions because of hydrolysis. These solutions may be studied by nuclear magnetic resonance methods to give information of the rate of exchange of EDTA between the free and complex-bonded states. A prerequisite for the method is that the concentration of free EDTA and the LnEDTA complex are of similar magnitude. The dominating species in the solutions used are the unhydrolysed complex and mono- and di-protonated EDTA.

The NMR spectra of complex-bonded EDTA may be of different type, depending on the configuration of the complex and on the lability of the bonds between EDTA and the central ion. Hence, the spectra may be used to obtain some structural information as well as some rate data.

Instrumental. The ^1H NMR spectra were recorded at 60 MHz, using a Varian A 60 A spectrometer. The shifts were measured with the usual side band technique by means of a Hewlett Packard audio frequency oscillator, model 202, and a frequency counter, model 5216 A.

The shifts are given relative to tetramethylsilane, TMS, which was used as an external reference. No corrections for bulk susceptibilities were made.

All spectra were recorded at the probe temperature, measured by the methanol shift. The temperature was found to be 44.9 ± 0.3 °C. Dissolved oxygen was removed from the solutions just before recording the spectra.

Kinetics of the lanthanum EDTA exchange. When studying the exchange between the diamagnetic complex and the free ligand, it is

favourable to have both these species in about equal concentrations. In order to obtain a large signal to noise ratio, concentrations in the order of 0.5 M are desirable. However, this was impossible in the present investigation because of the limited solubility of both the lanthanum complex and the free EDTA. The following solutions of varying pH were used:

$$\left\{ \begin{array}{ll} 50 \text{ mM} & \text{LaEDTA} \\ 50 \text{ mM} & \text{EDTA} \\ I = 1.0 \text{ M} & (\text{KCl}) \end{array} \right.$$

The hydrogen ion concentration was adjusted by 1 M potassium hydroxide. In these solutions, the ionic strength was chosen as 1.0 M instead of 0.5 M, since the large concentrations of ligand would otherwise make the major contribution to the ionic strength, a contribution which also varies strongly with the pH of the solution.

Fig. 7.1 a shows the spectra of free EDTA and the lanthanum EDTA complex in the absence of exchange. This was established by lowering the pH of the solutions until the line widths did not narrow any more. The peaks labelled A result from the protons in the acetate group of EDTA and those labelled B arise from the protons in its ethylene group. Indices F and C are used for free and complexed EDTA, respectively. A large signal in the spectra originates from a 50 Hz overtone to the water signal, corresponding to the frequency of the main current. This is due to the high amplification of the spectrometer, which is necessary because of the low EDTA concentrations.

The resolution of the spectrometer was adjusted so that the same linewidth (~ 0.6 Hz) was always obtained from the water signal. Each spectrum was recorded at least twice.

The hydrogen ion concentration was measured at 25 °C with the cell given above, but at an ionic strength of 1.0 M instead of 0.5 M.

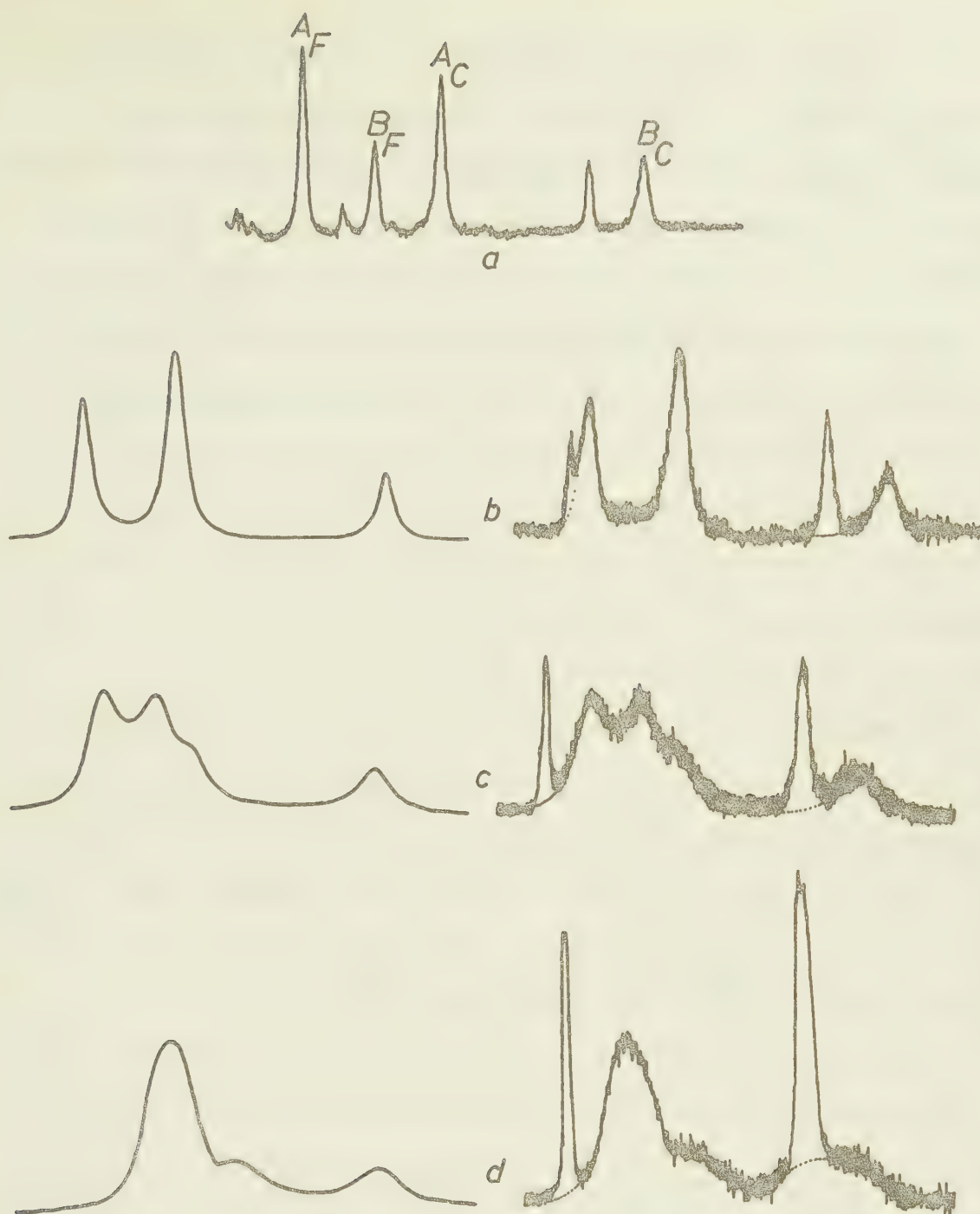


Fig. 7.1. Recorded and calculated spectra of free EDTA and lanthanum EDTA complex in about equal concentrations.

a) No exchange, b) $\tau_F = 0.153$ s, c) $\tau_F = 0.052$ s, and d) $\tau_F = 0.035$ s.

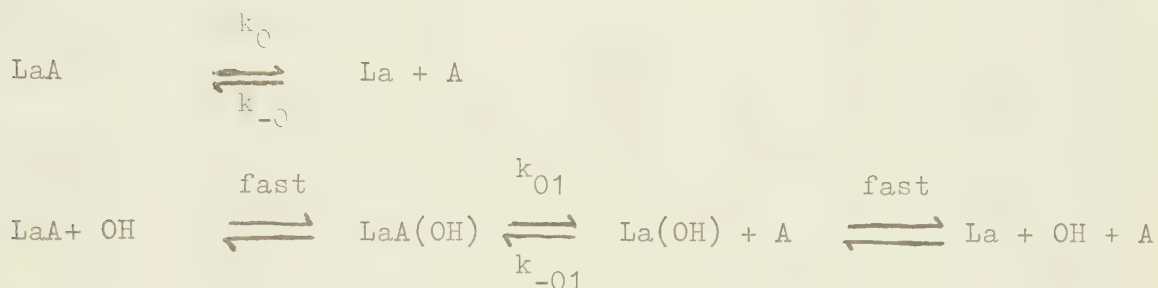
Calculation. Instead of using the approximative formulae for exchange processes, which can lead to rather large systematic errors²⁹, the mean lifetime of the free EDTA, τ_F , was calculated by line shape analysis. The exchange pattern can be described as two overlapping two-site cases, where each site shows a singlet. To make use of an available computer program, the present exchange case was treated as an AMX problem, where the shifts between A_F and B_F and between A_C and B_C , respectively, have been regarded formally as coupling constants. By using the full expressions derived by Gutowsky and Holm³⁰, line shapes have been calculated by a computer. By means of an iterative computer procedure^{31,32}, the parameters were adjusted so as to give the least error square sum to the observed spectrum.

The recorded spectra were digitized by measuring the heights from the base line in steps of 0.5 Hz for 200 points. By this procedure it was possible to subtract the overtone peaks of the water signal when they did not interfere too much. However, these "extra" signals limited the useful range of exchange rates. For lifetimes less than 0.036 s it was impossible to obtain any reliable results.

The following parameters have been adjusted in the calculations: K , a normalizing constant, τ_F , the mean lifetime of free EDTA, p_A , the population of free EDTA, and the "coupling" constants J_1 and J_2 , *i.e.* the shifts between A_F and B_F and between A_C and B_C , respectively. The transverse relaxation times, T_{2F} and T_{2C} , were determined from the line widths of the four peaks in the absence of exchange. Thus, T_{2F} for the signals A_F and B_F was found to be 0.187 s and 0.188 s, respectively, whereas T_{2C} for the peaks A_C and B_C showed a greater difference, *viz.* 0.159 s and 0.146 s. The mean value of T_{2C} , 0.153 s, was used in the calculations.

In Fig. 7.2, the adjusted values of J_1 , i.e. the shift between the acetate and ethylene protons in free EDTA, are plotted vs. the hydroxide ion concentration. The adjustment of the parameters was repeated with fixed values of J_1 taken from the curve $J_1([OH^-])$. The results of the calculations are given in Table 7.1. Some examples of calculated and recorded spectra are given in Fig. 7.1 b-d.

The reaction mechanism. The following reactions are regarded:



The first and the last steps in the hydroxide ion dependent path are rapid equilibria. The constants for the two equilibria are defined by

$$K_{\text{LaA(OH)}} = \frac{[\text{LaA(OH)}]}{[\text{LaA}][\text{OH}]} \quad \text{and} \quad K_{\text{L(OH)}} = \frac{[\text{La(OH)}]}{[\text{La}][\text{OH}]} ; \quad (7.1)$$

At equilibrium the rate equation becomes

$$-\frac{d[\text{LaA}]}{dt} = k_0[\text{LaA}] - k_{-0}[\text{La}][\text{A}] + k_{01}[\text{LaA(OH)}] - k_{-01}[\text{La(OH)}][\text{A}] = 0 ; \quad (7.2)$$

Combination of equations 7.1 and 7.2 gives

$$[\text{LaA}] (k_0 + k_{01} K_{\text{LaA(OH)}}) = [\text{A}] (k_{-0}[\text{La}] + k_{-01} K_{\text{L(OH)}} [\text{La}][\text{OH}]) \quad (7.3)$$

Fig. 7.2. The shift between the acetate and ethylene protons in free EDTA, as a function of the hydroxide ion concentration.



Table 7.1 Experimental and calculated data
for the EDTA exchange of LaEDTA.

J_1/Hz	τ_F/s	p_F	τ_C/s	$[\text{OH}] \cdot 10^8/\text{M}$
16.9	0.299	0.521	0.275	1.56
17.5	0.254	0.498	0.256	2.06
17.6	0.203	0.461	0.237	2.20
18.1	0.153	0.488	0.160	2.85
18.5	0.172	0.480	0.187	3.35
19.1	0.105	0.513	0.0995	5.33
19.2	0.0858	0.479	0.0932	5.40
19.2	0.0644	0.502	0.0639	7.46
19.3	0.0522	0.500	0.0523	8.73
19.3	0.0522	0.505	0.0512	9.21
19.4	0.0435	0.500	0.0435	11.0
19.4	0.0348	0.492	0.0360	13.6

$$\text{Thus } \frac{[\text{LaA}]}{\tau_C} = \frac{[\text{A}]}{\tau_F} \quad (7.4)$$

$$\text{where } \tau_C^{-1} = k_0 + k_{01} K_{\text{LaA}(\text{OH})} [\text{OH}]$$

$$\text{and } \tau_F^{-1} = [\text{La}] (k_{-0} + k_{-01} K_{\text{La}(\text{OH})} [\text{OH}])$$

Hence, τ_C^{-1} is a linear function of the hydroxide ion concentration.

The line shape analysis gives τ_F , but τ_C is related to τ_F by the following expression:

$$\frac{p_F}{\tau_F} = \frac{p_C}{\tau_C} \quad (7.5)$$

Figure 7.3 shows τ_C^{-1} as a function of the hydroxide ion concentration. From this graph the following constants of the dissociation rate are obtained.

$$k_0 = 0 \pm 1 \text{ s}^{-1} \text{ and } k_{01} \cdot K_{\text{LaA}(\text{OH})} = (2.0 \pm 0.4) 10^8 \text{ s}^{-1} \text{ M}^{-1}$$

The error given is the confidence limit on the 99% level of significance.

Merbach and Gnägi¹⁹ give a value of $K_{\text{LaA}(\text{OH})} < 1000 \text{ M}^{-1}$. Hence, the rate constant $k_{01} > (2.0 \pm 0.4) 10^5 \text{ s}^{-1}$ for the dissociation of the hydrolysed complex, $\text{La}(\text{OH})\text{EDTA}$.

Labilities of the coordination bonds. In free EDTA, the four ethylene protons and the eight acetate protons are equivalent within each group, and thus two singlets of relative intensities 1:2 are observed in the proton NMR spectrum. When complexing EDTA with a metal ion, different signal patterns will be obtained, depending on the lability of the metal-oxygen and the metal-nitrogen bonds, and on the structure of the complex.

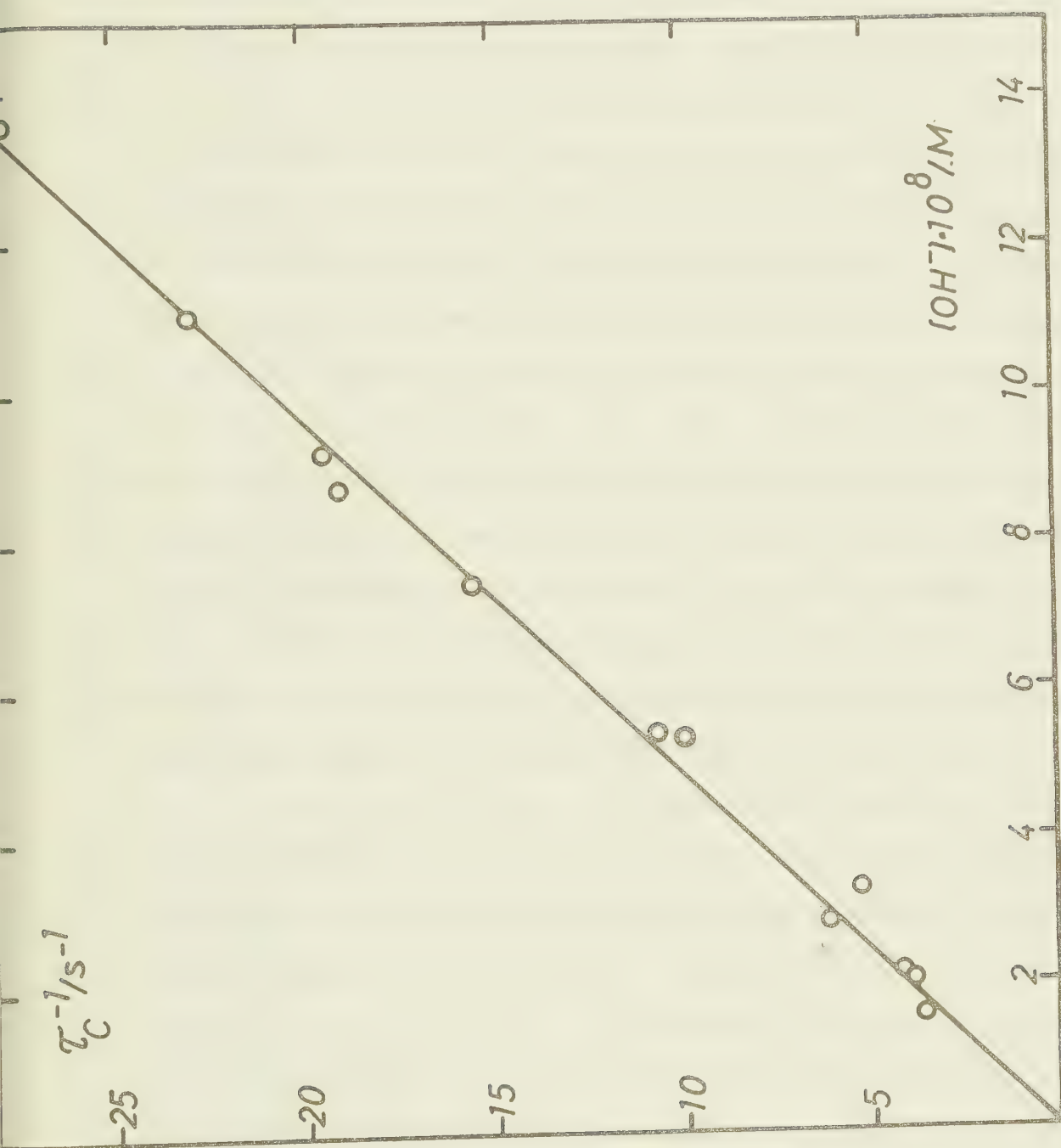


Fig. 7.3. The observed rate constant, τ_c^{-1} , as a function of the hydroxide ion concentration.

Reilly et al.³³ have given an excellent discussion of the four possible cases for an octahedral complex, viz: i) The lifetimes of both the metal-oxygen and metal-nitrogen bonds are short, ii) The lifetime of the metal-oxygen bond is short, while that of the metal-nitrogen bond is long, iii) The reversed situation; the lifetime of the metal-oxygen bond is long and that of the metal-nitrogen bond is short, and iv) The lifetimes of both bonds are long.

Hoard et al.³⁴ have determined the structure of the solids $\text{La}(\text{OH}_2)_4(\text{EDTA})\text{H}$ and $\text{M La}(\text{OH}_2)_5\text{EDTA}$ by X-ray diffraction. The lanthanum ion coordinates with four oxygen and two nitrogen atoms. The plane through the lanthanum and the two nitrogen atoms forms a quasi-mirror plane for the coordinated ligand. The ethylenediamine group in the ligand is slightly puckered.

If the ethylenediamine group is approximately planar, then the four ethylene protons all have the same magnetic environment, due to symmetry. Hence, they give one singlet, independent of the lifetime of the metal-oxygen bond. If, on the other hand, the group is puckered, these protons have different magnetic environments. This will give rise to a multiplet signal if the lifetime of the metal-oxygen bond is long, or a singlet if the lifetime of the bond is short.

The two protons on an acetate group are not magnetically equivalent. Thus, if the metal-nitrogen bond has a long lifetime, an AB-type multiplet of the acetate signal would occur, whereas for a short lifetime an average singlet signal is expected.

In view of the structure of the lanthanoid EDTA complexes, it is not very likely that the metal-nitrogen bond is broken without a preceding break of the metal-oxygen bonds on the coordinated acetate groups. Hence, a situation with a labile metal-nitrogen bond and a metal-oxygen bond of long lifetime seems very unlikely.

The ^1H NMR spectrum of the lanthanum EDTA complex consists of two singlets (Fig. 7.1 a). Thus, the lanthanum-nitrogen and lanthanum-oxygen bonds are both labile, since the puckered ring structure seems to be the most probable one.

Spectra of a solution containing about 180 mM lutetium EDTA complex were recorded in the pH range $2 < \text{pH} < 12$. Outside this range precipitation occurs. It was not necessary to add neutral salt to obtain information about the labilities of the bonds. The pH of the solution was varied by adding 1 M potassium hydroxide. The hydrogen ion concentration was determined with the cell given above, but using an ionic strength of 0.2 M in the reference half cell.

For the lutetium complex, the signal from the acetate protons is split into an AB quartet (Fig. 7.4). This indicates a metal-nitrogen bond of long lifetime. The metal-oxygen bond, on the other hand, probably has a short lifetime, since the ethylene protons give rise to a singlet. However, when the pH of the solution is increased to about 12 the AB pattern gradually disappears and a singlet appears. Furthermore, the chemical shifts for both the acetate protons and the ethylene protons change in this pH range (Table 7.2). This might be due to the formation of a mixed complex, viz. $\text{Lu}(\text{OH})\text{EDTA}$. The change in shift of the ethylene protons is about twice as large as that of the acetate protons. For this and for structural reasons, it is probable that the hydroxide ion is bound directly to the metal in the complex. This of course means a strong interaction with the metal-nitrogen bonds, which are labilized, and so giving rise to a singlet instead of an AB quartet.

From the measured shifts the equilibrium constant, $K_{\text{LnA}(\text{OH})}$, (eqn. 7.1) for the formation of the mixed lutetium EDTA hydroxide complex could be estimated to be about 100 M^{-1} , in accordance with the estimate given by Merbach and Gnägi ¹⁹.

Fig. 7.4. The recorded spectrum of 180 mM lutetium EDTA complex.

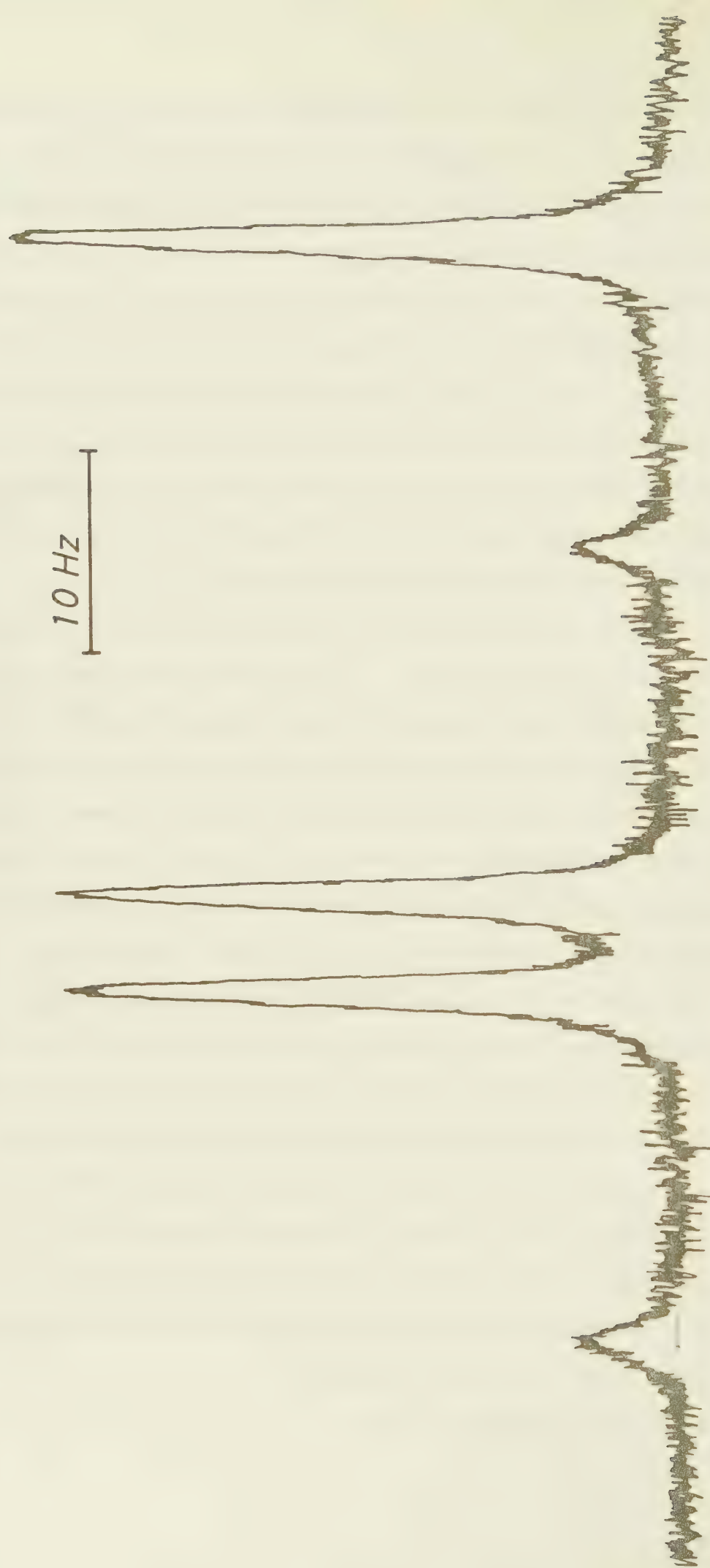


Table 7.2 The chemical shifts for acetate, Ac, and ethylene, Et, protons of the lutetium complex. Reference TMS.

$-\delta_{\text{Ac}}$ ppm	$-\delta_{\text{Et}}$ ppm	pH
3.62	3.04	1.98
3.62	3.04	2.55
3.62	3.04	3.19
3.63	3.05	3.76
3.63	3.04	4.29
3.62	3.04	6.43
3.61	3.04	6.96
3.63	3.04	8.24
3.61	3.04	9.16
3.62	3.04	9.86
3.60	3.01	10.60
3.57	2.95	11.47
3.55	2.92	12.22

The coupling constant for the AB quartet was calculated by the procedure given in ref 35, and was found to be $(17.1 \pm 0.3)\text{Hz}$.

Chapter 8

DISCUSSION

The rate law of exchange reactions. The rate law for the gross reaction



can be described fairly well by the proposed model. The expression for the observed rate constant is

$$k_{\text{obs}} = \left(\frac{f'}{1 + \frac{f}{f''} \delta_1} + f^D \frac{C_M}{f_M} \right) \frac{1 + \delta_2}{f_{\text{LA}}} \quad (8.1)$$

$$\text{where } \delta_1 = \frac{\beta_L}{\beta_M} \cdot \frac{f_M}{f_L} \cdot \frac{C_L}{C_M}$$

$$\text{and } \delta_2 = \frac{C_{\text{LA}}}{C_M} + \frac{\beta_L}{\beta_M} \cdot \frac{C_L + C_{\text{MA}}}{C_M} \cdot \frac{f_M}{f_L} \cdot \frac{f_{\text{LA}}}{f_{\text{MA}}}$$

All the notations are given in chapter 2.

The best condition to determine the dissociation rate, f' , of a complex, LA, is to have the concentration of LA small and a large excess of the exchanging metal ion M. This results in small values of δ_1 and δ_2 if the quotient β_L/β_M is not too large. However, when the metal ion L and its complex LA are in large excess over the exchanging metal ion M, the rate determining reaction is the d i s s o c i a t i o n of the complex of the exchanging metal MA, i.e. one of the backward reactions in the scheme on p. 6. Among others, D'Olieslager and Choppin¹⁸ have used these conditions for the reaction

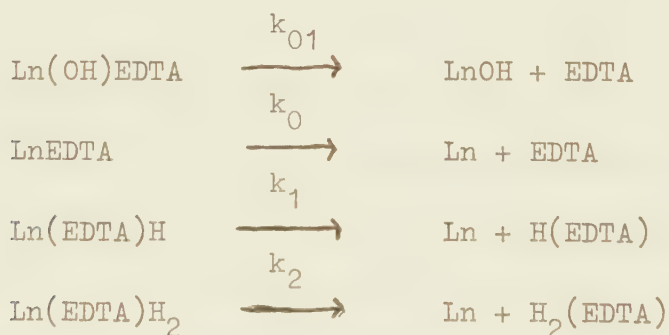


which obeys the experimental rate law

$$-\frac{d[\text{Eu}]}{dt} = k \frac{[\text{H}][\text{LaEDTA}]}{[\text{La}]} \cdot [\text{Eu}]$$

This is just a special case of the rate law described by equation 8.1. By dividing their rate constant with the quotient $\beta_{\text{Eu}}/\beta_{\text{La}}$, almost the same value of the dissociation rate for the europium complex is obtained as in the present paper (see Table 8.1). The rate law has also been checked by using large concentrations of both lanthanum ions and lanthanum complex together with a small concentration of copper ions. This gives large values of δ_1 and δ_2 in the rate equation. The resulting constants of f' agree with the previously determined rate constants for the copper system.

The mechanism of dissociation. The dissociation of EDTA from the lanthanoid EDTA complexes is catalysed both to hydrogen ions and hydroxide ions. The hydrogen ion catalysis proceeds over two parallel path-ways, viz. via complexes, containing either a monoprotinated or a diprotinated ligand, whereas the path catalysed by hydroxide ions proceeds over the hydroxo complex.



The acid and hydroxo complexes are all in rapid equilibrium with each other.

According to Hoard et al. ³⁴, the proton in $\text{La}(\text{EDTA})\text{H}$ is bound to one of the four non-coordinating carboxylate oxygens. The configuration of the complex makes it impossible for any of the nitrogen atoms to bind a proton. Presumably, this is also the case for the second proton in the diprotonated complex, which thus also is bound to a carboxylate oxygen. The association and dissociation of a proton to the complex is a rapid process compared to the dissociation of the ligand. This is confirmed by the NMR spectra at pH 2, where the concentrations of nonprotonated and monoprotonated complexes of lutetium EDTA are about equal. If the proton-oxygen bond were not labile, a separate signal from this proton would be seen. Such a peak is not observed. Only the average signal from the fast exchange of protons between the water and the complex has been detected. Some authors ^{12,16,18} have proposed a mechanism, where the association of protons to the complex is a slow process followed by a rapid dissociation of the ligand. This mechanism is not very probable; one reason, among others, is given above.

The ^1H NMR spectra show that the metal-oxygen bonds have short lifetimes both in the rapidly dissociating lanthanum complex and in the much slower dissociating lutetium complex. The metal-nitrogen bond has a long lifetime in the lutetium complex, but is labile in the lanthanum complex. Hence, the rate determining factor of the dissociation seems to be the metal-nitrogen bond cleavage. The same conclusion has been drawn by Margerum ²¹ from exchange reactions of copper and nickel with EDTA and with hydroxyethylethylenediaminetriacetate. The association of protons to the complex thus labilizes the metal-nitrogen bonds.

A hydroxo complex is formed by dispelling one proton from a coordinated water molecule in the hydrated complex. This is a fast reaction. The hydroxide ligand labilizes the metal-nitrogen bonds more than the associated proton, presumably because it is bound directly to the metal ion. In accordance with this, the rate constant for the hydroxide catalysed path is several orders of magnitude faster than that for the reaction catalysed by hydrogen ions via the monoprotinated species.

By substitution of water molecules in the lanthanoid EDTA complex, it is possible to coordinate a second ligand, thus forming a mixed complex. Acetate ions accelerate the dissociation of the EDTA complex to a small extent Chapter 6,¹⁶. Brucher and Szilágyi²⁰ found from exchange reactions with copper that glycolate ions increase the dissociation rate of the terbium EDTA complex to a considerable extent. Acetate ions have a much lower affinity to lanthanoid ions than have glycolate ions. The concentration of the mixed acetate complex is much smaller than that of the mixed glycolate complex at similar concentrations of acetate and glycolate. Both these ligands are presumably bound directly to the metal ion in the mixed lanthanoid complexes. Their ability to increase the dissociation rates may then be due to a labilization of the metal-nitrogen bonds in the EDTA complex, i.e. an effect similar to that of the hydroxide ion.

Variations of the dissociation rates with the ionic radii of the lanthanoid ions. In Table 8.1, the rate constants from this investigation have been collected together with the values from other authors. The constants given for the pathways catalysed by hydrogen ions and hydroxide ions are products of the constant K_{LnAH_n} and $K_{LnA(OH)}$ for the corresponding complex and the true rate constant. Kolat and Powell²⁴

Table 8.1. The rate constants of dissociation of lanthanoid EDTA complexes. The constants $\bar{k}_{01}$, $\bar{k}_1$, and $\bar{k}_2$ contain the equilibrium constants for the corresponding complexes.

Ln	k_0/s^{-1}	$\bar{k}_1/\text{s}^{-1} \text{ M}^{-1}$	$\bar{k}_2/\text{s}^{-1} \text{ M}^{-2}$	t °C	ref.
La	$(2.0 \pm 1.0)10^{-2}$	$(3.7 \pm 0.5)10^3$	$(1.9 \pm 0.7)10^6$	25	
	-	$7.0 \cdot 10^3$	-	25	10
Ce	-	$1.6 \cdot 10^3$	-	20	16
	-	$1.8 \cdot 10^3$	-	20	17
	-	$5.5 \cdot 10^3$	-	25	11
Pr	$(9.0 \pm 7.5)10^{-3}$	$(1.6 \pm 0.1)10^3$	$(1.0 \pm 0.4)10^6$	25	
	-	$1.7 \cdot 10^3$	-	25	11
Nd	-	$(1.09 \pm 0.04)10^3$	$(7.0 \pm 1.5)10^5$	25	
	-	$6.6 \cdot 10^2$	-	20	17
	-	$1.08 \cdot 10^3$	-	25	10
Eu	-	$(4.5 \pm 0.7)10^2$	$(2.8 \pm 1.5)10^6$	25	
	-	$6.0 \cdot 10^2$	-	22	18
Gd	-	87	$6.0 \cdot 10^6$	20	17
Tb	-	31	$9.5 \cdot 10^5$	20	17
Dy	-	12.5	$5.8 \cdot 10^5$	25	10
Ho	-	12.8	-	24	14
Er	-	8.9 ± 0.5	$(7.7 \pm 0.7)10^4$	25	
Yb	-	0.76 ± 0.08	$(1.43 \pm 0.07)10^4$	25	
	-	0.70	$2.5 \cdot 10^4$	25	10
Lu	-	0.52	$5.4 \cdot 10^3$	20	17

$$\text{La} \quad \bar{k}_{01} = (2.0 \pm 0.4)10^8 \text{ s}^{-1} \text{ M}^{-1}$$

$$t = 45 \text{ } ^\circ\text{C}$$

The errors given are the confidence limits on the 99% level of significance.

have reported such constants for almost all the monoprotonated lanthanoid complexes. The logarithm of these constants have values between 2.5 and 2.8. Some tentative values of the stepwise constants $K_{\text{LnAH}_2}/K_{\text{LnAH}}$ for the diprotonated complexes have been reported by Brucher and Szarvas^{13,17} to be in the range $(0.1 - 0.2) \text{ M}^{-1}$. It is likely that the constants K_{LnAH_2} for the diprotonated complexes do not change more than those for the monoprotonated complexes along the lanthanoid series. The constant, $K_{\text{LaA}(\text{OH})}$, for the hydroxo EDTA complex of lanthanum is estimated to be less than $1\,000 \text{ M}^{-1}$ ¹⁹. Because of the lack of accurate values of these constants, no calculations of the true rate constants have been done.

In Fig. 8.1, $\log \bar{k}_1$ and $\log \bar{k}_2$ have been plotted vs. the inverse ionic radius of the lanthanoid ions. The rate constants obtained by the methods in this investigation are on the whole in accordance with those obtained from radiochemical exchange studies of the reactions.

Both curves show an irregularity, viz. for $\bar{k}_1$ in the region dysprosium to erbium and for $\bar{k}_2$ between neodymium and gadolinium. Geier and Karlen⁸ found a corresponding behaviour of the rate constant for the nonprotonated complexes reacting with oxyquinoline-5-sulfonate in the region of samarium to terbium. They have also carried out some spectrophotometric measurements on europium EDTA complexes at varying temperatures⁷. They claim that the temperature dependence of the spectra is due to the existence of two kinds of complexes, viz. $\text{Ln}(\text{EDTA})(\text{H}_2\text{O})_3^-$ and $\text{Ln}(\text{EDTA})(\text{H}_2\text{O})_2^-$, which are in equilibrium with each other. The one with three water molecules predominates in the beginning of the series, whereas the dihydrated complex is favoured at the end of the series. Hoard et al.³⁴ have found four water molecules coordinating to the lanthanum ion in the solid $\text{LaH}(\text{EDTA})(\text{H}_2\text{O})_4$.

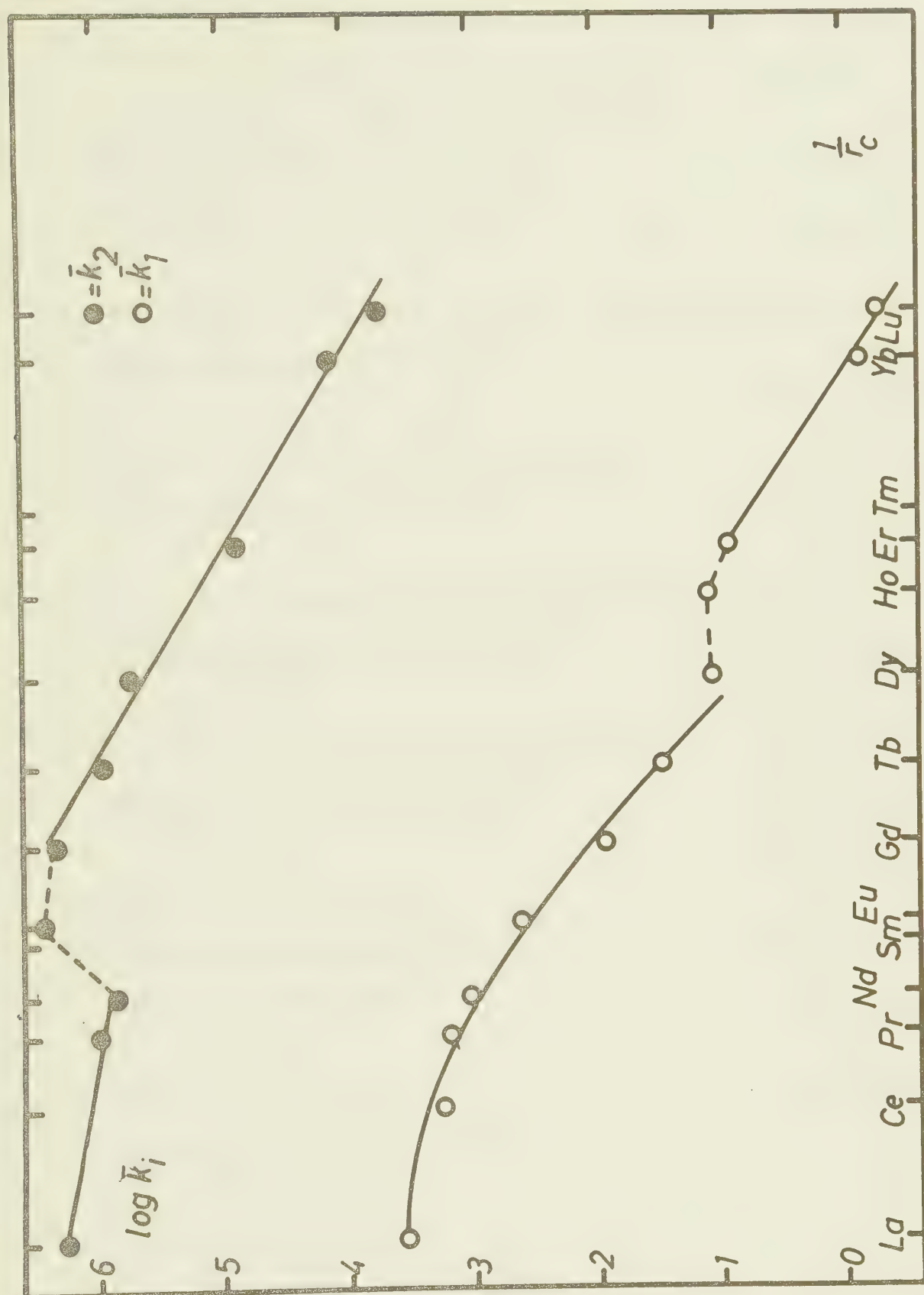


Fig. 8.1. $\log \bar{k}_2$ and $\log \bar{k}_1$, as a function of the inverse ionic radius of the lanthanoid ions.

On the grounds given above, one may conclude that the two regions with monotoneous changes of the rate constants in each of the two curves correspond to complexes with different numbers of coordinated water molecules. Thus, the monoprotonated complexes might have four coordinated water molecules in the beginning of the series and three water molecules at the end.

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A P P E N D I X

An ALGOL program for the
rate equations of the
kinetic model.

by

Carl-Gustav Ekström

and

Torsten Ryhl

In order to handle the rather complex and time-consuming calculations, resulting from the kinetic model, developed in Chapter 2, a high-speed computer ALGOL program has been written.

From the kinetic model the following expressions for the observed rate constant can be deduced (Chapter 2 and ref 20).

$$k_{\text{obs}} = \left(\frac{f'}{1 + \frac{f'}{f''} \delta_1} + f^D \frac{C_M}{f_M} \right) \delta_2 \quad (1)$$

$$\text{where } \delta_1 = \frac{\beta_L}{\beta_M} \cdot \frac{C_L}{C_M} \cdot \frac{f_M}{f_L}$$

$$\text{and } \delta_2 = \frac{1}{f_{LA}} \left(1 + \frac{C_{LA}}{C_M} + \frac{\beta_L}{\beta_M} \cdot \frac{C_L + C_{MA}}{C_M} \cdot \frac{f_M}{f_L} \cdot \frac{f_{LA}}{f_{MA}} \right)$$

The symbols have the following meanings:

L = the metal of that system for which the rate constants are to be determined.

M = the metal of the exchanging system

A = the ligand,

k_{obs} = the observed rate constant, f' , f'' and f^D are functions of the hydrogen ion concentration, h , of the general type

$$i = \frac{\sum_{i=0}^Q a_i h^i}{1 + \sum_{j=1}^r b_j h^j}$$

where a_i and b_j are parameters which contain the rate constants.

The quantity f' is the rate of dissociation for the complexes of the investigated system, f'' the corresponding function for the exchanging system, and f^D the rate for the substitution path II. Each function has its own limits of summation.

The quantity f_L is a hydrogen ion dependent function, connected with the hydroxocomplexes $L(OH)_{N_x}$,, $L(OH)$.

$$f_L = \sum_{i=0}^{N_x} K_{x,i} \frac{1}{h^i}$$

$$\text{where } K_{x,i} = \frac{[L(OH)_i][H^+]^i}{[L]}$$

The quantity f_{LA} is a hydrogen ion dependent function for the mixed hydroxo and proton complexes of the type



$$f_{LA} = \sum_{i=0}^{N_y} K_{y,i} \frac{1}{h^i} + \sum_{j=1}^{N_z} K_{z,j} h^j$$

$$\text{where } K_{y,i} = \frac{[L(OH)_i A][H]^i}{[LA]}$$

$$\text{and } K_{z,j} = \frac{[LAH_j]}{[LA][H]^j}$$

β_L is the stability constant for the formation of LA

$$\beta_L = \frac{[LA]}{[L][A]}$$

f_M , f_{MA} , and β_M correspond to f_L , f_{LA} , and β_L for the exchanging system, M. C_i = concentration of the species "i" at equilibrium.

PRINCIPLES OF THE PROGRAM

Principles of calculation. The constants of the functions f' and f^D can be calculated by means of the method of least squares when the values of the functions f' and f^D of all experimental points: (k_{obs}, h) have been first determined.

The general principle of the calculation is easier to describe for a case where $\delta_1 f'/f'' \ll 1$ (eq. 1.).

By introducing the notations $k_{\text{obs}}/\delta_1 = k$ and $C_M/f_M = C$, equation 1 is reduced to $k = f' + f^D C$. (2)

From two points with the same h - but with different C -values, the value of f^D can be determined:

$$\begin{cases} k_1 = f' + f^D C_1 \\ k_2 = f' + f^D C_2 \end{cases} \quad (3)$$

which gives

$$f^D = \frac{k_1 - k_2}{C_1 - C_2} \quad (4)$$

One of the points chosen is directly experimentally determined, whereas the other one is a value from a reference curve. This reference curve is computed by a least square method from a series - the reference series - of experimental observations at constant values of C .

This calculation of f^D is performed for each experimental point outside the reference series. Thus, a set of corresponding values of f^D and h is obtained, from which the parameters in the function are calculated.

A value of f' is then calculated for each experimental point.

$$f' = k - f^D \cdot C \quad (5)$$

where the value of f^D is evaluated from the above determined constants of f^D . From this set of f' (h)-values, the parameters of f' are calculated.

The general case, based on equation 1, without approximations results in eqn(6):

$$\frac{1}{k_1 - C_1 f^D} - \left(\frac{\delta_1}{f''} \right)_1 = \frac{1}{k_2 - C_2 f^D} - \left(\frac{\delta_1}{f''} \right)_2 \quad (6)$$

from which the value of f^D is solved. Because of the experimental errors in the k_{obs} -values not only positive solutions to equation 6 may occur, but sometimes also negative and imaginary ones. The imaginary f^D -values are rejected, but not the negative ones. Hence, the distribution becomes less biased.

The expression 5 in the general case becomes

$$f' = \frac{k - C f^D}{1 - \left(\frac{\delta_1}{f''} \right) [k - C f^D]} \quad (7)$$

The expressions 6 and 7 contain the function f'' , i.e. the dissociation rate of the exchanging system. If the constants of f'' are known from other experiments the calculation is straight forward. If, on the other hand, the constants of f'' are unknown, an iterative procedure has to be used (p.A:8). In this procedure, f'' is regarded as known in equations 6 and 7 at each iteration step.

Weighting functions for f^D and f' . The constants of the different functions are determined by minimizing the error square sum

$$F = \sum_i (y_{\text{obs}} - y_{\text{calc}})^2 w_i$$

where w_i is the weight of each observation. Considering normal distributed random errors of y_{obs} , the weight should be proportional to $1/\sigma_y^2$, where σ_y is the standard deviation of the y_{obs} -values.

The error in f^D . Assuming that the random errors of all variables except the ones of k_{obs} are negligible, and that the relative error in k_{obs} is constant over the h range, one may obtain the absolute error in f^D by differentiation of equation 6.

$$\left| df^D \right| = \left| \frac{\left(\frac{k_{\text{obs}}}{\delta_2} \right)_p + \left(\frac{k_{\text{obs}}}{\delta_2} \right)_{\text{ref}} \cdot Q}{C_p - C_{\text{ref}} \cdot Q} \right| \cdot \left| \frac{dk_{\text{obs}}}{k_{\text{obs}}} \right| \quad (9)$$

$$\text{where } Q = \frac{\left(\frac{k_{\text{obs}}}{\delta_2} \right)_p - C_p \cdot f^D}{\left(\frac{k_{\text{obs}}}{\delta_2} \right)_{\text{ref}} - C_{\text{ref}} \cdot f^D} ;$$

$$\text{Then } \sigma_{f^D} = \text{constant} \cdot \left| df^D \right|. \quad (10)$$

However, f^D is not known initially, but has to be determined by an iterative procedure. In this way a set of "best" constants in the least-squares sense are obtained.

The expression for Q can also be written

$$Q = \frac{1 + \frac{f'}{f''} (\delta_1)_{\text{ref}}}{1 + \frac{f'}{f''} (\delta_1)_p} \quad (11)$$

Thus $Q \approx 1$ when either δ_1 or f'/f'' is small.

The error in f' . Regarding only the constant relative error of k_{obs} , one obtains the error in f' by differentiation of equation 7.

$$\left| df' \right| = \left| \frac{dk_{\text{obs}}}{k_{\text{obs}}} \right| \cdot \left(1 + \frac{\delta_1}{f''} f' \right)^2 \cdot \frac{k_{\text{obs}}}{\delta_2} \quad (12)$$

$$\text{and thus } \sigma_{f'} = \text{constant} \cdot \left| df' \right|. \quad (13)$$

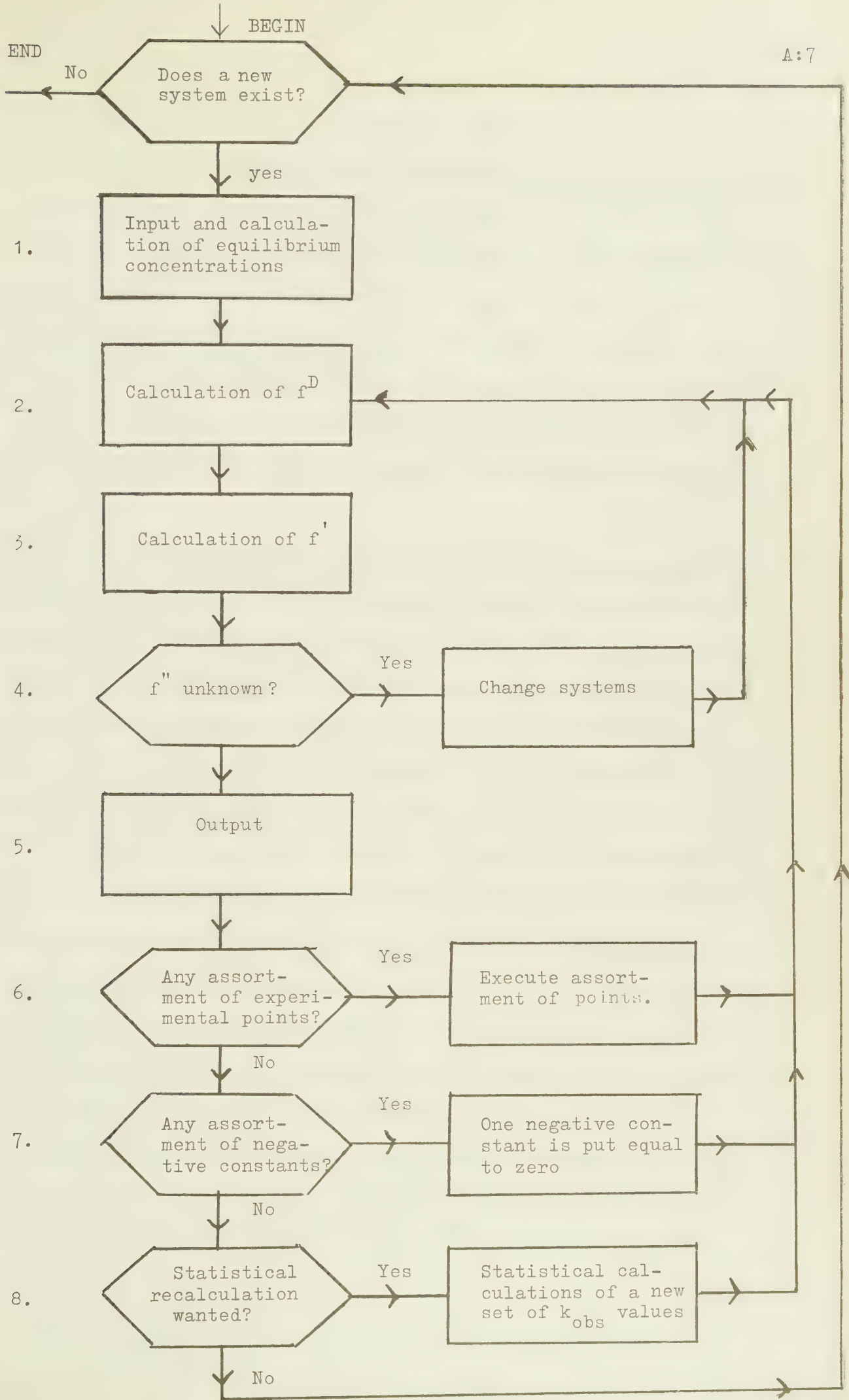
The adjustment of the curve is performed by an iterative procedure.

Weights for non-normal points. If some of the points differ much more than the normal errors from the "correct" values, the resulting curve will be of "bad" fit. The following empirical weighting function has been constructed in order to reduce the influence of such points. The calculated standard deviation has been multiplied with $(1 + n_p \Delta y)$, where n_p is the number of points and Δy the relative distance to the calculated curve, thus giving a weight proportional to $1/[(1 + n_p \cdot \Delta y) \sigma_y]^2$. This weight function has been used in the case of f^D for points differing more than 100% from the "true" value and for f' for points differing more than a value given in the input.

The program. Fig. 1 gives a block scheme of the program in outline.

1. Input. This part reads the input data of the system and calculates the equilibrium concentrations by means of general equilibrium relations.

The input begins with name and stability constants of the investigated system as well as the stability constants of the exchanging system. The total concentrations are given. This information is followed by the measured pairs of observed rate constants and hydrogen ion concentrations. If f'' is unknown the corresponding data of the exchanging system are read and treated.



2. Calculation of f^D . The value of the function f^D is calculated from equation 6 for all points not belonging to the reference series. A curve is fitted to the values by the method of least-squares, using the weight function given above. From the first set of constants obtained in this way, new weights are calculated. These are used to a new curve fitting sequence and so on. This iterative procedure is interrupted when the sum of the absolute relative changes of the constants between two succeeding loops is less than 10^{-3} .
3. Calculation of f' . The value of f' is calculated from equation 7 for all points. The used values of f^D are calculated from the constants in the preceding section. If f'' is unknown δ_1/f'' is put equal to zero in the first step. The weight for each point is evaluated by equation 13. Since the weights are dependent on the final "correct" f' values (eqn. 12), a similar iterative procedure is used as has been described for f^D above. The iteration procedure is interrupted when the sum of the absolute relative changes of the constants is less than 10^{-3} between two succeeding loops.
4. Changing systems. If f'' is not known, an exchange of the two systems is performed. This means that the former exchanging system is treated as the investigated system and the former investigated system acts as the corresponding exchanging system. The former approximative value obtained for f' is now used as f'' and the calculation is performed as before. New exchanges between the two systems are repeated until the sum of the absolute relative changes of the constants of both f' and f^D is less than 10^{-4} in both systems.

5. Output. The output from the program is placed at this point for several reasons. At this stage the calculations of f' and f^D are finished. Thus, when any of the special procedures following later on in the program are used, it is possible to obtain outputs before and after each such new procedure.
6. Assortment of experimental points. It is possible to assort experimental points, which differ more than a specified percentage, given in the input data, from the calculated curve. After the points have been excluded in the block 6, a complete recalculation is made from block 2.
7. Assortment of negative constants. The following procedure to assort negative constants can be specified in the input. If one or more of the calculated constants have negative values, one of the constants is given the value zero and a complete recalculation from block 2 is made. The constant set equal to zero is the one that has the largest index in one of the functions. One of the functions f' and f^D is first searched for negative parameters, viz. that one which contains most terms. The next step is then to search the remaining function for negative constants. Then the corresponding functions of the exchanging system are searched in the sequence obtained above.
8. Statistics. By this procedure it is possible to calculate new constants of f' and f^D from a slightly different set of k_{obs} -values. The new k_{obs} -values are obtained by multiplying the experimental k_{obs} -values with a set of random factors. These are normally distributed with the mean value 1 and a σ -value given in the input.

The program

This program is written in the ALGOL programming language. The program contains some specialities not included in ALGOL 60. The differences from ALGOL 60 are those of the UNIVAC 1108 ALGOL, which are specified in Table 1. Fig. 2 gives a detailed block scheme of the program.

Read number of systems
and maximum number of H^+
and OH^- complexes

More systems
to treat?

No → END

Yes

KORT 2: Read number of
points in the system

KORT 2 A: Read name of system; $\log\beta$; β_H and β_{OH}
if any; specifications of: assortment of points,
statistical recalculation, assortment of nega-
tive constants, functions f' and f^D ; name of ex-
changing system; $\log\beta$; β_H and β_{OH} if any, speci-
fication of: function f'' .

VARV = 0

Printing of input data

Read C_L^O , C_A^O , C_M^O ,
 σ_{obs} for artificial k_{obs}
and H values. Speci-
fication of one reference
series for f^D

Artificial data
wanted?

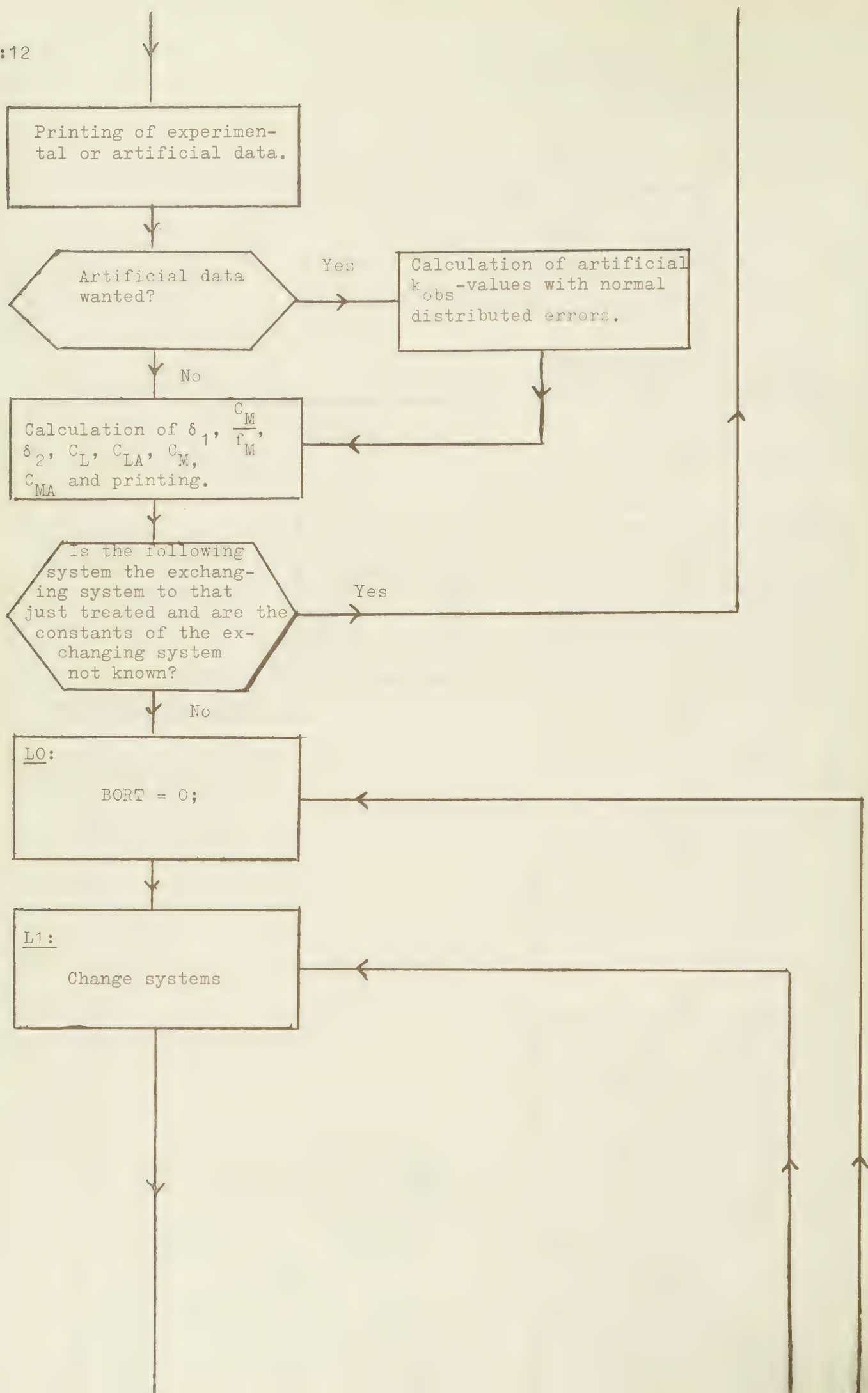
Yes

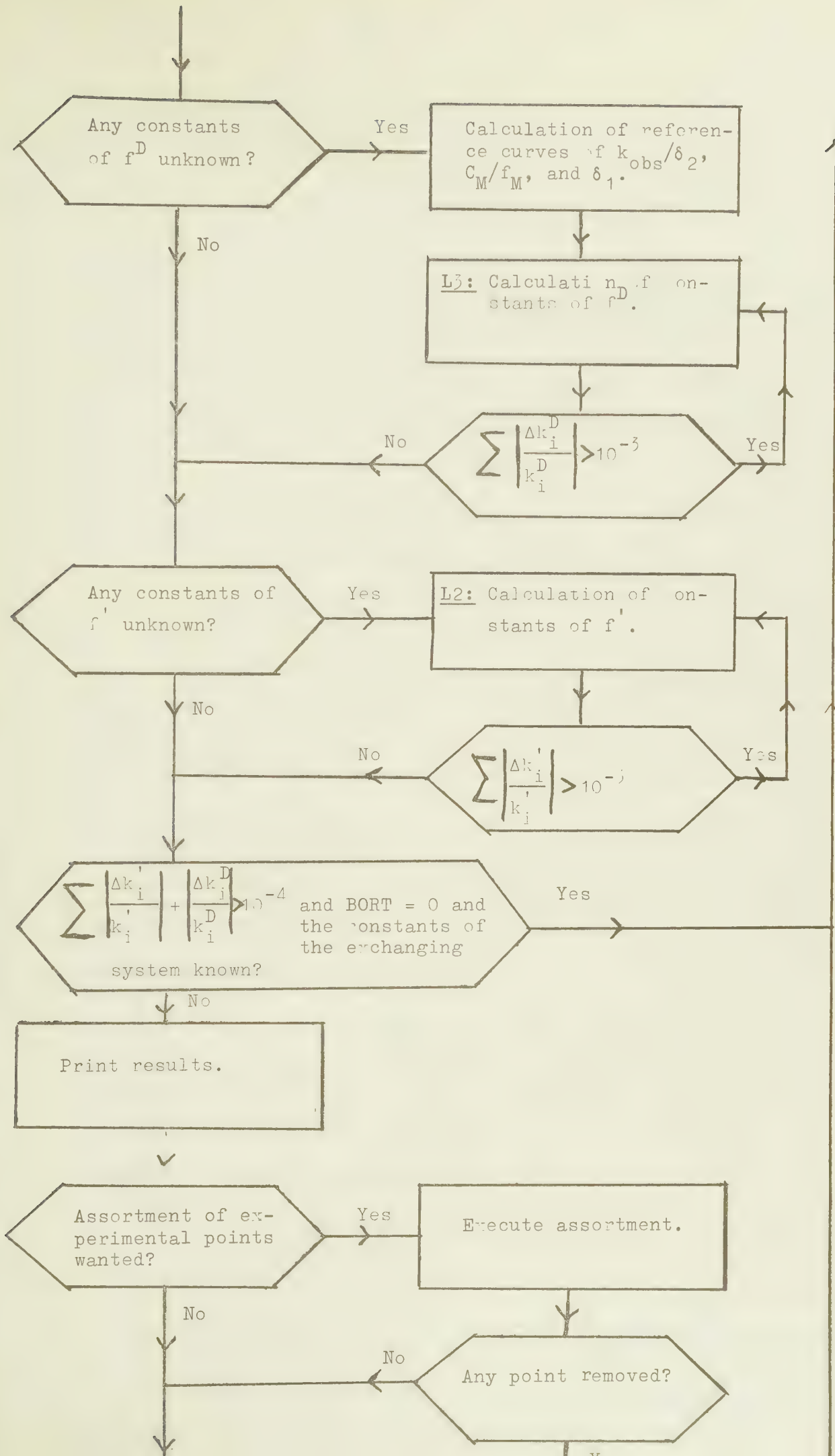
Read specification for
artificial H-values.
Produce artificial H-
values.

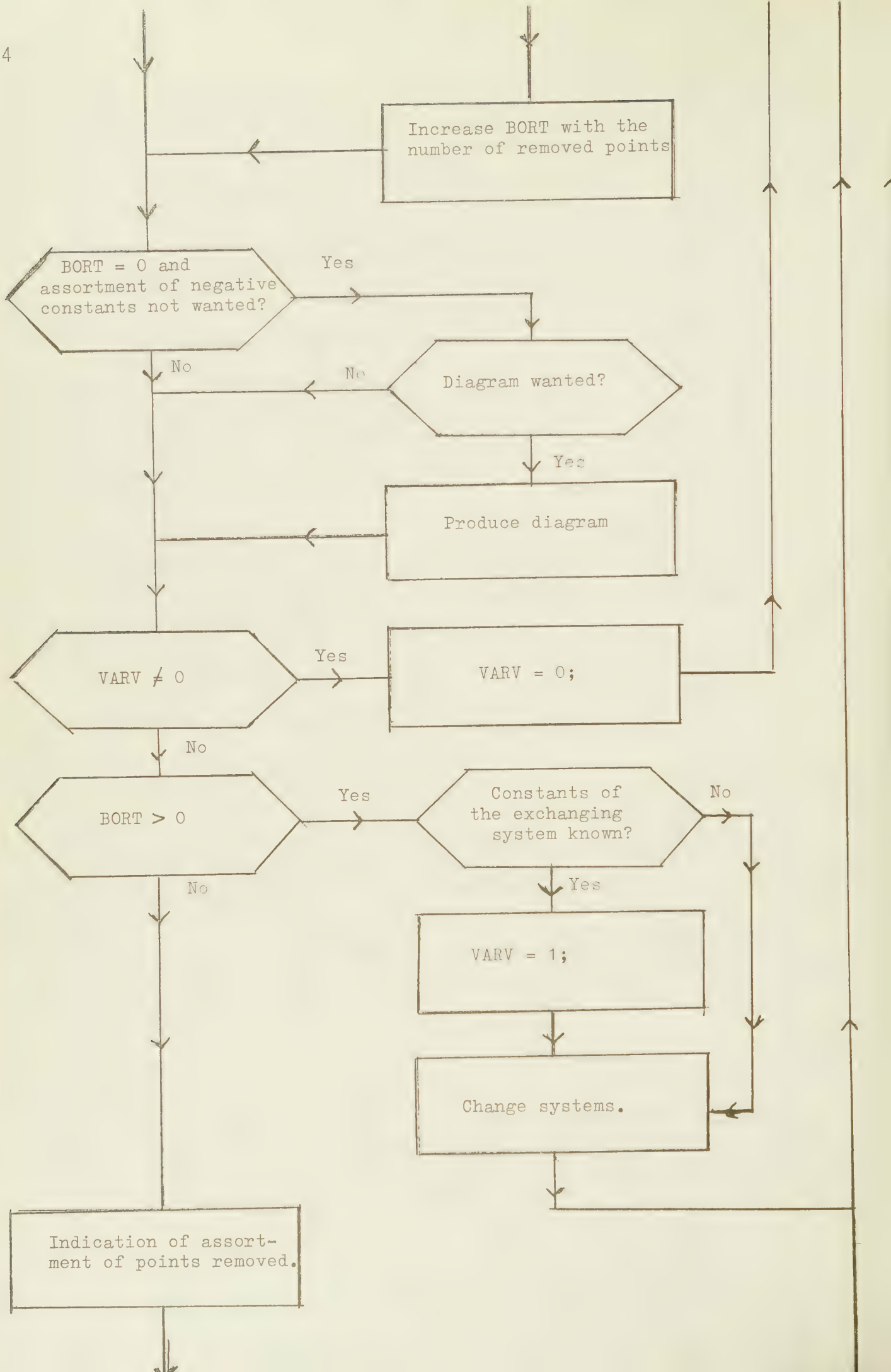
No

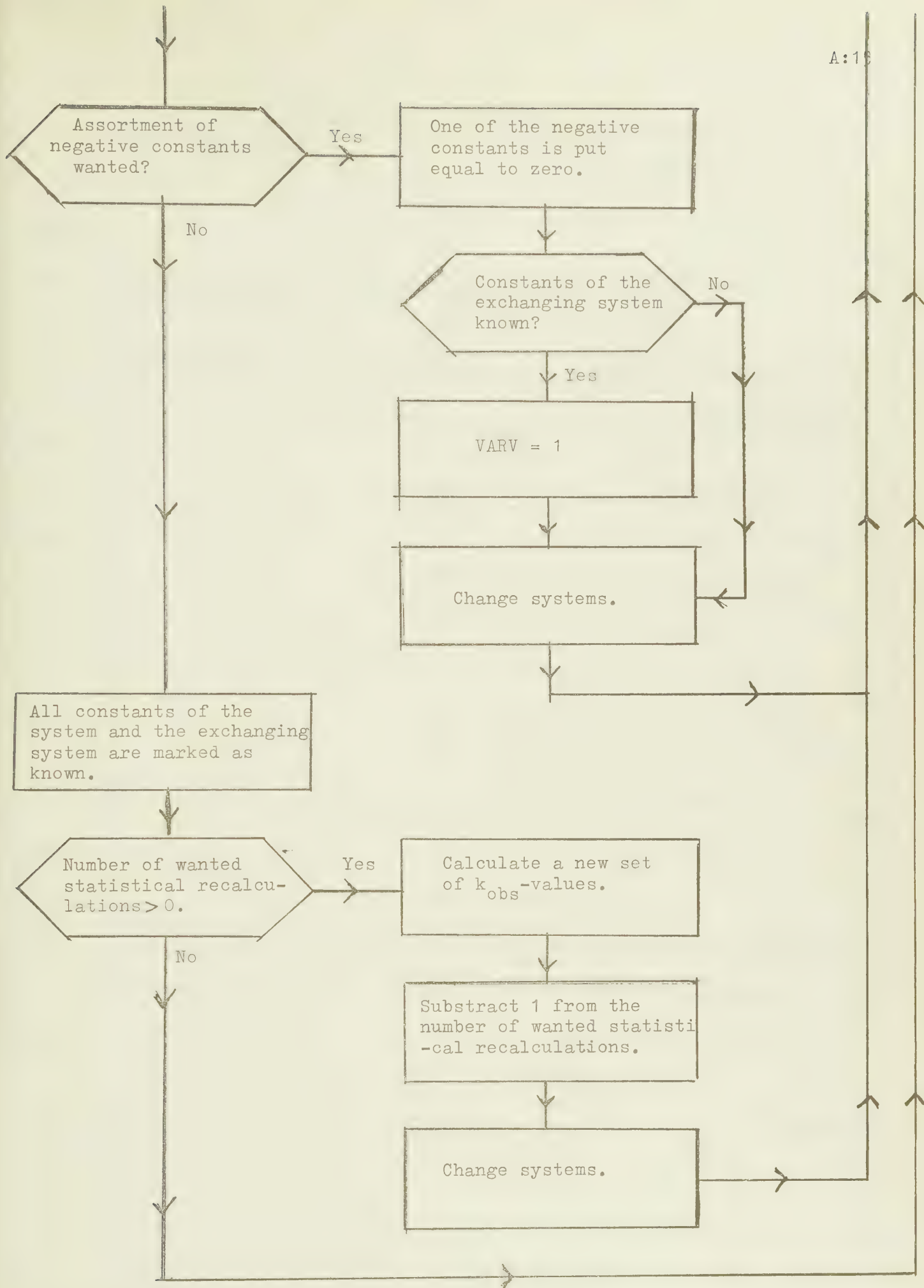
Read pairs of experi-
mental H and k_{obs}

Read the constants of
 f' , f^D , and f'' .









Differences in notations and extensions
to ALGOL 60

Table 1.

N o t a t i o n s	
UNIVAC 1108 ALGOL	ALGOL 60
*	x
//	÷
**	↑
=	:=
LSS	<
LEQ	≤
EQL	=
GEQ	≥
GTR	>
NEQ	≠
OR	∨
AND	∧
FOR I = (1, 1, N) DO	for I:= 1 step 1 until N do

Differences in notations and extensions
to ALGOL 60

Table 1.
continued

E x t e n s i o n s t o A L G O L 6 0	
UNIVAC 1108 ALGOL	Explanation
REAL 2	Double precision 10^{-308} < N < 10^{308} maximum 18 digitis.
XOR	Exclusive disjunction $\neg(A \equiv B)$.
LIST	The LIST declaration defines an ordered sequence of ex- pression.
LOCAL	A LOCAL declaration is re- quired to resolve all forward references to indentifiers.
CLOCK	Present time in seconds. Integer.
MAX	The algebraic largest element of a list. Real.
MIN	The algebraic smallest element of a list. Real.

BEGIN

PROCEDURE EKSYST(A,N,UT);

INTEGER N; REAL 2 ARRAY A; LABEL UT;

BEGIN INTEGER R,RB,L,K;

REAL 2 DELTA,TEST,EPS,BYT;

REAL 2 ARRAY B[1:N,1:N], C[0:2*N];

EPS = 7.0_{10}^{-18} ; BYT = 1.0_{10}^{-10} ;

FOR R = (1,1,N) DO FOR K = (1,1,N) DO

B[R,K] = IF K EQL R THEN 1 ELSE 0;

FOR R = (1,1,N) DO BEGIN RB = R;

NYRAD: C[0] = A[R,0];

FOR K = (1,1,N) DO BEGIN

C[K] = A[R,K];

C[N+K] = B[R,K] END;

FOR K = (1,1,R) DO IF A[R,K] NEQ 0 THEN BEGIN

FOR L = 0, (K+1,1,N) DO BEGIN

A[R,L] = A[R,L]/A[R,K];

IF K NEQ R THEN BEGIN

DELTA = A[R,L] - A[K,L];

IF L LEQ R AND L GTR 0 THEN BEGIN

TEST = ABS(DELTA)/(ABS(A[R,L]) + ABS(A[K,L]));

IF TEST LSS EPS THEN DELTA = 0 ELSE

IF TEST LSS BYT THEN GO TO BYTRAD END;

A[R,L] = DELTA END END;

IF K EQL R THEN FOR L = (1,1,N) DO

B[R,L] = B[R,L]/A[R,K]

ELSE FOR L = (1,1,N) DO

B[R,L] = B[R,L]/A[R,K] - B[K,L] END

ELSE IF K EQL R THEN

```

BYTRAD: BEGIN RB = RB + 1;

      IF RB LEQ N THEN BEGIN

        FOR K = (0,1,N) DO BEGIN

          A[R,K] = A[RB,K];

          A[RB,K] = C[K] END;

        FOR K = (1,1,N) DO BEGIN

          B[R,K] = B[RB,K];

          B[RB,K] = C[N + K] END;

        GO TO NYRAD END

      ELSE WRITE('NO SOLUTION EXISTS');

      GO TO UT END END;

FOR R = (1,1,N - 1) DO FOR K = (R + 1,1,N) DO BEGIN

  FOR L = 0, (K + 1,1,N) DO A[R,L] = A[R,L] - A[R,K] * A[K,L];

  FOR L = (1,1,N) DO B[R,L] = B[R,L] - A[R,K] * B[K,L] END;

FOR R = (1,1,N) DO FOR K = (1,1,N) DO A[R,K] = B[R,K] END;

PROCEDURE MKMEKV(NP,Y,A,SY,N,V,NF, INDF, KF,X,SX,DY,S,UT);

  INTEGER NP,N,V,NF;

  REAL S;

  INTEGER ARRAY INDF;

  REAL ARRAY Y,A,SY,KF,X,SX,DY;

  LABEL UT;

  BEGIN INTEGER I,J,K,RT,RF,TID;

    REAL FM,FW,BBER,SUMMA,Z;

    REAL ARRAY F[0:N], HJ,XJ[1:N], W[1:NP], B[0:N,1:NP];

    REAL 2 ARRAY E[1:N, 0:N];

```

```

TID = CLOCK;
FOR K = (1,1,N) DO HJ[K] = 1;
FOR J = (1,1,NF) DO HJ[INDF[J]] = 0;
FOR I = (1,1,NP) DO BEGIN
    DY[I] = 0;
    FOR K = (1,1,N) DO B[K,I] = A[K,I];
    B[0,I] = Y[I];
    FOR J = (1,1,NF) DO B[0,I] = B[0,I] - KF[J] * B[INDF[J], I] END;
FOR K = (0,1,N) DO BEGIN
    FM = MAX (FOR I = (1,1,NP) DO ABS (B[K,I]));
    F[K] = MIN (FOR I = (1,1,NP) DO IF B[K,I] EQL 0 THEN FM
        ELSE ABS (B[K,I]));
    F[K] = SQRT (FM) * SQRT (F[K]) END;
FOR I = (1,1,NP) DO FOR K = (0,1,N) DO B[K,I] = B[K,I]/F[K];
Z = IF S EQL 0 THEN 1 ELSE S;
IN: FOR I = (1,1,NP) DO BEGIN
    SUMMA = ABS (DY[I]/(Y[I] - DY[I]));
    W[I] = (1 + IF SUMMA LEQ Z THEN 0 ELSE NP * SUMMA) *
    IF V EQL - 1 THEN ABS (Y[I] - DY[I]) ELSE
    IF V EQL 1 THEN 1 ELSE SY[I] END;
FM = MAX (FOR I = (1,1,NP) DO W[I]);
FW = MIN (FOR I = (1,1,NP) DO
    IF W[I] EQL 0 THEN FM ELSE W[I]);
FOR I = (1,1,NP) DO
    W[I] = FM/IF W[I] EQL 0 THEN FW ELSE W[I] ** 2/FW;
FOR K = (1,1,N) DO FOR J = (0,1,N) DO BEGIN
    E[K,J] = 0;
    FOR I = (1,1,NP) DO E[K,J] = E[K,J] + B [K,I] * B[J,I] * W[I] END;

```

```

IF NF NEQ 0 THEN BEGIN
  FOR K = (1,1,NF) DO E[1,INDF[K]] = 0;
  RT = 0;
  FOR RF = (1,1,N) DO IF E[1,RF] NEQ 0 THEN BEGIN
    RT = RT + 1;
    IF RF GTR RT THEN BEGIN
      FOR K = (1,1,N) DO E[K,RT] = E[K,RF];
      FOR K = (0,1,N) DO E[RT,K] = E[RF,K] END END END;
EKSYST (E, N-NF, UT);
IF NF NEQ 0 THEN BEGIN
  RF = N-NF;
  FOR RT = (N,-1, RF+1) DO
    IF HJ[RT] EQL 1 THEN BEGIN
      FOR K = (1,1,N) DO E[K,RT] = E[K,RF];
      FOR K = (0,1,N) DO E[RT,K] = E[RF,K];
      RF = RF -1 END
    ELSE BEGIN
      FOR K = (1,1,N) DO E[K,RT] = E[RT,K] = 0;
      E[RT,0] = 0 END END;
S = 0;
FOR I = (1,1,NP) DO BEGIN
  BBER = 0;
  FOR K = (1,1,N) DO BBER = BBER + B[K,I] * E[K,0];
  S = S + W[I] * (B[0,I] - BBER) ** 2;
  DY[I] = F[0] * (B[0,I] - BBER) END;
S = IF NP - N EQL 0 THEN 0 ELSE SQRT (S/(NP + N));
SUMMA = 0;

```

```

FOR K = (1,1,N) DO BEGIN
    X[K] = E[K,0] * F[0]/F[K];
    SX[K] = SQRT(ABS(E[K,K, ])) * S * F[0]/F[K];
    IF X[K] NEQ 0 THEN SUMMA = SUMMA + ABS(XJ[K]/X[K] - 1);
    XJ[K] = X[K] END;
IF CLOCK - TID GTR 10 THEN
    WRITE ('TIME EXCEEDED') ELSE
IF SUMMA/(N - NF) GTR 110 -4 THEN GO TO IN;
IF V EQL 1 THEN S = S * F[0];
FOR J = (1,1,NF) DO X [INDF[J]] = KF[J] END;

REAL PROCEDURE FKT(L,T,N,K,H);
    INTEGER L,T,N;
    REAL H;
    REAL ARRAY K;
    BEGIN INTEGER I;
        REAL ST,SN;
        ST = IF T EQL 0 THEN 0 ELSE K[T];
        FOR I = (T -1,-1,1) DO ST = ST * H + K[I];
        SN = IF N EQL T THEN 0 ELSE K[N];
        FOR I = (N -1,-1,T+1) DO SN = SN * H + K[I];
        FKT = H ** L * ST/(1 + H * SN) END;

PROCEDURE EKTVA (A,B,C,X1,X2,UT);
    REAL A,B,C,X1,X2;
    LABEL UT;
    BEGIN IF A EQL 0 THEN BEGIN
        IF B EQL 0 THEN GO TO UT ELSE
        BEGIN X1 = X2 = -C/B; GO TO SLUT END END;
        IF B EQL 0 THEN BEGIN X1 = -C/A;
            IF X1 LSS 0 THEN GO TO UT;

```



```

      X1 = SQRT(X1);  X2 = -X1;

      GO TO SLUT END;

      X1 = 4 * A * C/B/B;

      IF X1 GTR 1 THEN GO TO UT;

      X2 = B * (1 + SQRT(1 - X1))/2;

      X1 = -X2/A;  X2 = -C/X2;

SLUT:  END;

REAL PROCEDURE TF(N,NK,ALFA);

      INTEGER N,NK;

      REAL ALFA;

      BEGIN INTEGER I,NY;

      REAL Y,D,X,T;

      I = NY = N - NK;

      D = 110 - 2;

      Y = ALFA * SQRT(NY) *

      IF NY // 2 * 2 EQL NY THEN 1 ELSE 1.5707963;

      FOR I = I - 2 WHILE I GEQ 1 DO

          Y = Y * I/(I + 1);

      FOR T = T + D WHILE X LSS Y DO

          X = X + D * (1 + (T - D/2) ** 2/NY) ** (-(NY + 1)/2);

      TF = T - 1.5 * D END;

EXTERNAL PROCEDURE RANF;

COMMENT THIS PROCEDURE GIVES RECTANGULAR

DISTRIBUTED PSEUDO-RANDOM NUMBERS IN THE

INTERVALL 0 - 1;

```

```
EXTERNAL PROCEDURE RITA;

COMMENT THIS PROCEDURE DRAWS A DIAGRAM
OF THE EXPERIMENTAL POINTS AND THE
CALCULATED CURVE BY MEANS OF A PLOTTER;
```

```
REAL PROCEDURE SLUMP;
```

```
BEGIN REAL A,D,X,Y;

  FOR A = RANF[0] -0.5 WHILE ABS(A) GTR 0.49 DO;

    D = 0.01; X = 3.1;

    Y = (0.499 - ABS(A)) * 2.5066;

    FOR X = X - D WHILE Y GTR 0 DO

      Y = Y - D/6 * (EXP(-((X - D) ** 2/2)) +

        4 * EXP(-((X - D/2) ** 2/2)) +

        EXP(-(X * X)/2));

      SLUMP = SIGN(A) * (X + 1.5 * D) END;
```

```
PROCEDURE TYP (G,P,K,NR,J);
```

```
  INTEGER NR,J;

  INTEGER ARRAY G,P;

  REAL ARRAY K;

  BEGIN INTEGER I;

    REAL ARRAY KFIX[1:10];

    READ (FOR I = (1,1,4) DO KFIX[I]);

    FOR I = 1,2,3 DO G[NR,J,I] = KFIX[I];

    K[NR,J,0] = -KFIX[4];

    IF K[NR,J,0] LSS 0 THEN BEGIN

      READ(FOR I = (1,1, -K[NR,J,0]) DO

        (P[NR,J,I], KFIX[I]));

      FOR I = (1,1, -K[NR,J,0]) DO

        K[NR,J,P[NR,J,I]] = KFIX[I] END;

      IF K[NR,J,0] EQL - G[NR,J,3] THEN K[NR,J,0] = 1 END;
```

```

INTEGER      AFORM, BORT, DNR, EJKLAR, G11, G12, G13, G21, G22, G23,
              GW1, GW2, GW3, I, I1, ISORT, ISTK, ISYST, J, JO, J1, J2,
              J3, JSTK, KORRKONST, N, NFIX, NFL, NFLA, NP, NPSEER, NR, NS,
              REFDATA, REFNR, RN, SYSTDATA, SYSTNR, TID1, VARV, W;

REAL         A, AP, AR, BP, BR, CANOLL, CL, CLA, CLNOLL, CM, CMA, CMNOLL,
              CP, CR, DP, DR, EOF, FBISS, FDE, FDK, FL, FLA, FM, FMA,
              FPK, FPRIM, H, HFAK, KFAK, KOB, L, LOGB, M, Q, Q1, Q2,
              S, SIGD, SIGP, SUMMA, SYNT, X1, X2;

STRING       SYST[3], REF[3];

BOOLEAN      BOL;

```

```

      READ(NS,NFL,NFLA,AFORM);

      IF NFL LSS 1 THEN NFL = 1;

      IF NFLA LSS 1 THEN NFLA = 1;

```

```

BEGIN

      INTEGER ARRAY DATAFEL[1:NS + 1], XSORT, DIAG, XNEG, CMSRT[1:NS],
      INDFIX[0:6], STK[1:NS,1:4],
      G[1:NS,1:2,1:3], P[1:NS,1:2,1:6];

      REAL ARRAY      B, SIGMA, SIGXX[1:NS], KFIX[1:6], KD, KK, KM, KP,
                      KQ, KR, SKD, SKP[1:10], BFL[1:NS,0:NFL],
                      BFLA[1:NS,0:NFL + NFLA], TFAK[1:2,0:4],
                      K[1:NS,1:2,0:10];

      STRING ARRAY    NAMN[3:1:NS + 1];

      LOCAL LABEL     UTHOPP;

      LIST             LUT1(NAMN[SYSTNR], NAMN[NR],
                          SYSTDATA, LN(B[SYSTNR])/LN(10),
                          LN(B[NR])/LN(10),
                          FOR I = (-NFL,1,NFLA) DO I,
                          FOR I = (0,1,NFL) DO BFL[SYSTNR,I],
                          FOR I = (0,1,NFL+NFLA) DO BFLA[SYSTNR,I],

```

```

FOR I = (0,1,NFL) DO BFL[NR,I],
FOR I = (0,1,NFL+NFLA) DO BFLA[NR,I],
FOR J = 1,2,3 DO (FOR I = 1,2 DO G[SYSTNR,I,J],
FOR I = (1,1, IF BOL THEN 1 ELSE 0) DO
    G[NR,1,J]),
FOR J = 1,2, DO FOR I = (1,1, IF K[SYSTNR,J,0]
    EQL 1 THEN G[SYSTNR,J,3] ELSE
    IF K[SYSTNR,J,0] EQL 0 THEN 0 ELSE
    - K[SYSTNR,J,0]) DO (P[SYSTNR,J,I],
    K[SYSTNR,J,P[SYSTNR,J,I]]),
FOR I = (1,1, IF BOL THEN G[NR,1,3] ELSE 0) DO
(P[NR,1,I], K[NR,1,P[NR,1,I]]),
FOR I = (1,1, IF XSORT[SYSTNR] EQL 0 THEN 0 ELSE 1)
    DO XSORT[SYSTNR],
FOR I = (1,1, IF STK[SYSTNR,1] EQL 0 THEN 0 ELSE 1)
    DO STK[SYSTNR,1],
FOR I = (1,1, IF STK[SYSTNR,4] GTR 0 THEN 1 ELSE 0)
    DO STK[SYSTNR,4]/10,
FOR I = (1,1, IF STK[SYSTNR,3] GTR 0 THEN 1 ELSE 0)
    DO STK[SYSTNR,3]/10),
LUT1B (FOR I = (1,1,G[SYSTNR,1,3]) DO KP[I],
    FOR I = (1,1,G[SYSTNR,2,3]) DO KD[I],
    FOR I = (1,1,G[NR,1,3])DO KR[I]),
LUT5 (NAMN[NR], NAMN[RN],
    FOR I = (1,1, IF STK[NR,1] EQL 0 XOR
    STK[NR,2] EQL 0 THEN 1 ELSE 0) DO
(STK[NR,1], FOR J = (1,1, IF STK[NR,4] EQL 0
    THEN 1 ELSE 0) DO SIGXX[NR] * 100), J1,
    FOR I = (1,1,G[NR,1,3]) DO (I,K[NR,1,I],
    FOR J = (0,1,4) DO IF K[NR,1,I] EQL 0
    THEN 0 ELSE ABS(100 * TFAK[1,J] *
    SKP[I]/K[NR,1,I])), J2,

```

```

      FOR I = (1,1,G[NR,2,3]) DO (I,K[NR,2,I],
        FOR J = (0,1,4) DO IF K[NR,2,I] EQL 0 THEN 0
          ELSE ABS(100 * TFAK[2,J] * SKD[I]/K[NR,2,I])));

```

```

FOR I = (1,1,NS) DO BFL[I,NFL] = BFLA[I,NFL] = 1;
ISYST = 1;

```

```

KORT2: READ(SYSTDATA,UTHOPP);

```

```

BEGIN REAL ARRAY CREF[1:9,1:SYSTDATA];

```

```

KORT2A: SYSTNR = 0;

```

```

BEGIN INTEGER ARRAY UTPKT, NEGM[0:SYSTDATA];

```

```

REAL ARRAY CSYST[1:9,1:SYSTDATA];

```

```

LOCAL LABEL FEL, BER, VIA, SLUT;

```

```

KORT3: READ(SYST,LOGB,KORRKONST,REF,J,W,I1,J1,
  ISTK, JSTK, J2, N);

```

```

BOL = SYST EQL REF;

```

```

NAMN[ISYST] = SYST;

```

```

NR = ISYST;

```

```

ISYST = ISYST + 1;

```

```

FOR I = (1,1,ISYST -2) DO

```

```

  IF NAMN[I] EQL SYST THEN

```

```

    BEGIN NR = I; ISYST = ISYST -1 END;

```

```

  IF LOGB NEQ 0 THEN B[NR] = 10 ** LOGB;

```

```

  IF KORRKONST NEQ 0 THEN

```

```

    READ (FOR I = (0,1,NFL -1) DO BFL[NR,I],

```

```

      FOR I = (0,1,NFL -1),(NFL +1,1,NFL + NFLA) DO
        BFLA[NR,I]);

```

```

  IF SYSTNR EQL 0 THEN BEGIN

```



```

IF J LSS 0 THEN BEGIN
    READ (UTPKT[0]);
    READ (FOR I = (1,1,UTPKT[0]) DO UTPKT[I] END;
    XSORT[NR] = IF J EQL -99 THEN 0 ELSE ABS(J);
    DIAG[NR] = I1;
    IF J2 LSS 0 THEN BEGIN
        READ(NEGM[0]);
        READ(FOR I = (1,1,NEGM[0]) DO NEGM[I] ) END;
        XNEG[NR] = IF J2 EQL 0 OR J2 EQL -1 THEN 0 ELSE NR;
        CMSRT[NR] = N;
        STK[NR,1] = STK[NR,2] = J1;
        STK[NR,3] = ISTK;
        STK[NR,4] = JSTK;
        FOR J = 1,2 DO TYP(G,P,K,NR,J) END
    ELSE IF BOL THEN BEGIN
        TYP(G,P,K,NR,1);
        K[NR,2,0] = 1 END;
    IF SYSTNR EQL 0 THEN BEGIN
        SYSTNR = NR;
        GO TO KORT3 END;
    REFNR = NR;
    VARV = 0;
    WRITE(LUT1);

```

```

FOR J = (0,NPSER,SYSTDATA -1) DO BEGIN
  READ(NPSER,CLNOLL,CANOLL,CMNOLL,SYNT,HFAK,KFAK,FEL);
  IF HFAK EQL 0 THEN HFAK = 1;
  IF KFAK EQL 0 THEN KFAK = 1;
  FOR I = (J +1,1,ABS(NPSER) +J) DO BEGIN
    CSYST[1,I] = CLNOLL;
    CSYST[2,I] = CANOLL
    CSYST[3,I] = CMNOLL END;
  IF SYNT NEQ 0 THEN BEGIN
    READ (H,A);
    FOR I = (J +1,1,ABS(NPSER) + J) DO BEGIN
      CSYST[9,I] = I;
      CSYST[5,I] = 1+ IF SYNT LSS 0 THEN 0
      ELSE SLUMP * SYNT;
      IF A EQL 0 THEN CSYST[4,I] = (RANF[0] * 49 + 1)* H
      ELSE BEGIN
        CSYST[4,I] = H;
        H = IF A GTR 0 THEN H + A ELSE
        H * ABS(A) END END;
      WRITE (IF SYNT LSS 0 THEN 0 ELSE SYNT, J +1,ABS(NPSER)+J) END
    ELSE IF NPSER GTR 0 THEN BEGIN
      READ(FOR I = (J +1,1,NPSER +J) DO (CSYST[4,I],
        CSYST[5,I]), FEL);
      FOR I = (J +1,1,NPSER +J) DO BEGIN
        CSYST[9,I] = I;
        CSYST[4,I] = CSYST[4,I] * HFAK;
        CSYST[5,I] = CSYST[5,I] * KFAK END END END;

```

```

IF SYNT NEQ 0 THEN BEGIN
  READ (FOR I = (1,1,G[SYSTNR,1,3]) DO KP[I]);
  READ (FOR I = (1,1,G[SYSTNR,2,3]) DO KD[I]);
  READ (FOR I = (1,1,G[NR,1,3]) DO KR[I],FEL);
  WRITE (LUT1B) END;
WRITE (FOR I = (1,1,SYSTDATA) DO (I,FOR J = (1,1,5) DO
  CSYST[J,I]));
FOR I = (1,1,NEGM[0]) DO CSYST[3,NEGM[I]] = -ABS(CSYST[3,NEGM[I]]);
IF UTPKT[0] GTR 0 THEN BEGIN
  WRITE (FOR I = (1,1,UTPKT[0]) DO UTPKT[I]);
  FOR I = (1,1,UTPKT[0]) DO CSYST[4,UTPKT[I]] = 0;
  J = 0;
  FOR I = (1,1,SYSTDATA) DO
    IF CSYST[4,I] NEQ 0 THEN BEGIN
      J = J + 1;
      IF J NEQ I THEN FOR I1 = (1,1,9) DO
        CSYST[I1,J] = CSYST[I1,I] END;
      SYSTDATA = SYSTDATA - UTPKT[0] END;
      N = 4; L = 0;
OM:  FOR I = (1,1,SYSTDATA) DO BEGIN
      A = CSYST[N,I] * (1 - L);
      W = I;
      FOR J = (I + 1,1,SYSTDATA) DO
        IF ABS(CSYST[N,J]) LSS ABS(A) THEN BEGIN
          W = J;
          A = CSYST[N,J] * (1 - L) END;
      FOR J = (1,1,5), 9 DO KK[J] = CSYST[J,W];
      FOR J = (W - 1,-1,I) DO FOR J1 = (1,1,5), 9 DO
        CSYST[J1,J + 1] = CSYST[J1,J];
      FOR J = (1,1,5), 9 DO CSYST[J,I] = KK[J] END;

```

```

IF CMSRT[SYSTNR] GTR 0 THEN BEGIN
    L = CMSRT[SYSTNR]/1000;
    CMSRT[SYSTNR] = 0; N = 3; GO TO OM END;
READ (EOF,BER);
REP:  READ (EOF,FEL);
      GO TO REP;
FEL:  WRITE ('ERROR IN DATA');
VIA:  DATAFEL[SYSTNR] = SYSTNR;
      IF VARV NEQ 0 THEN DATAFEL[REFNR] = REFNR
          ELSE BEGIN      NR = SYSTNR;
              RN = REFNR END;
      GO TO SLUT;
BER:  IF DATAFEL[SYSTNR] NEQ DATAFEL[NR] THEN BEGIN
      WRITE ('REFERS TO A SYSTEM MARKED WITH ERROR'); GO TO VIA END;

FOR I = (1,1,SYSTDATA) DO BEGIN
    L = CSYST[1,I];
    A = CSYST[2,I];
    M = ABS(CSYST[3,I]);
    H = CSYST[4,I];
    FL = BFL[SYSTNR,NFL];
    FM = BFL[NR,NFL];
    FOR J = (NFL -1,-1,0) DO BEGIN
        FL = FL * H + BFL[SYSTNR,J];
        FM = FM * H + BFL[NR,J] END;
    FL = FL/H ** NFL;
    FM = FM/H ** NFL;
    FLA = BFLA[SYSTNR,NFL + NFLA];
    FMA = BFLA[NR,NFL + NFLA];
    FOR J = (NFL + NFLA -1,-1,0) DO BEGIN

```

```

      FLA = FLA * H + BFLA[SYSTNR,J];
      FMA = FMA * H + BFLA[NR,J] END;

FLA = FLA/H ** NFL;
FMA = FMA/H ** NFL;
Q = B[SYSTNR]/B[NR] * FM/FL * FLA/FMA;
Q1 = (Q - 1)/M/A;
Q2 = 2 * M * A/(M + A + Q * (L - A));
CMA = Q2/(1 + SQRT(1 + Q1 * Q2 ** 2) * SIGN(Q2));
CLA = A - CMA;
CL = L - CLA;
CM = M - CMA;
CSYST[1,I] = Q * FMA/FLA * CL/CM;
CSYST[6,I] = (CM + CLA + Q * (CL + CMA))/CM/FLA;
CSYST[3,I] = CM/FM * SIGN(CSYST[3,I]);
IF SYNT NEQ 0 THEN BEGIN
      FBISS = FKT(G[NR,1,1], G[NR,1,2], G[NR,1,3], KR, H);
      CSYST[5,I] = (1/(1/FKT(G[SYSTNR,1,1],
      G[SYSTNR1,2], G[SYSTNR1,3], KP, H) +
      IF FBISS EQL 0 THEN 0 ELSE
      CSYST[1,I]/FBISS) + ABS(CSYST[1,I]) *
      FKT(G[SYSTNR2,1], G[SYSTNR,2,2], G[SYSTNR,2,3],
      KD, H)) * CSYST[6,I] * CSYST[5,I] END;
IF STK[SYSTNR,1] GTR 0 THEN BEGIN
      CSYST[7,I] = CSYST[5,I];
      CSYST[8,I] = CSYST[4,I] END;
WRITE (CSYST[9,I], H, CL, CLA, CMA, CM
      FOR J = 1,3,6,5 DO CSYST[j,I]) END;

```



```

IF NR GTR SYSTNR AND K[NR,1,0] + K[NR,2,0] LSS 2 THEN
  BEGIN FOR I = (1,1,SYSTDATA) DO FOR J = (1,1,9) DO
    CREF[J,I] = CSYST[J,I];
    REFDATA = SYSTDATA;
    READ (SYSTDATA, UTHOPP);

  GO TO KORT2A END;

```

```

LO:  BORT = 0;
      TID1 = CLOCK;
      EJKLAR = 0;
L1:  NP = IF NR EQL SYSTNR THEN REFDATA ELSE SYSTDATA;
      FOR I = (1,1,10) DO KR[I] = K[NR,1,I];
      NR = IF NR EQL SYSTNR THEN REFNR ELSE SYSTNR;
      RN = IF NR EQL SYSTNR THEN REFNR ELSE SYSTNR;
      FOR I = (1,1,10) DO BEGIN
        KP[I] = K[NR,1,I];
        KD[I] = K[NR,2,I] END;
      G11 = G[NR,1,1];
      G12 = G[NR,1,2];
      G13 = G[NR,1,3];
      G21 = G[NR,2,1];
      G22 = G[NR,2,2];
      G23 = G[NR,2,3];
      IF G13 GEQ G23 THEN W = 1 ELSE W = 2;
      GW1 = G[NR,W,1];
      GW2 = G[NR,W,2];
      GW3 = G[NR,W,3];

```

```

BEGIN INTEGER ARRAY SORT[1:NP];

REAL ARRAY    YP, YD, D,  $\phi$ , YQ[1:NP],
              XP, XD[1:GW3,1:NP],
              C[1:9,1:NP];

LOCAL LABEL   IMA;

LIST LUT6(C[9,I], H, A, KOB, IF KOB LEQ 0
          THEN 0 ELSE (A/KOB -1) * 100, FPK, FPRIM,
          IF FPRIM LEQ 0 THEN 0 ELSE (FPK/FPRIM -1) * 100,
          FDK, FDE, IF FDE LEQ 0 THEN 0 ELSE
          (FDK/FDE -1) * 100);

FOR J = (1,1,9) DO FOR I = (1,1,NP) DO
  C[J,I] = IF NR EQL REFNR THEN CREF[J,I] ELSE CSYST[J,I];
J = 0;

FOR I = (1,1,NP) DO BEGIN
  H = C[4,I];
  M = C[3,I];
  S = C[5,I]/C[6,I];
  FBISS = C[2,I] = FKT(G[RN,1,1,], G[RN,1,2], G[RN,1,3], KR,H);
  IF M LSS 0 AND S NEQ 0 THEN BEGIN
    J = J +1;
    YP[J] = S;
    YQ[J] = C[1,I];
    YD[J] = -M;
    FOR I1 = (1,1,GW2) DO XP[I1,J] = H ** (GW1 + I1 -1);
    FOR I1 = (GW2 +1,1,GW3) DO XP[I1,J] = -S * H ** (I1 - GW2);
    FOR I1 = (1,1,GW3) DO XD[I1,J] = H ** (I1 -1) END END;
  IF J GEQ GW3 THEN BEGIN
    SIGP = 0.001;
    MKMEKV(J,YP,XP,D,GW3,- 1,0,INDFIX,KFIX,KK,SKP,D,SIGP,VIA);
    SIGD = 0.001;
  
```

```

MKMEKV(J,YQ,XD,D,GW3, -1,0,INDFIX,KFIX,KQ,SKD,D,SIGD,VIA);
SIGD = 0.001;
MKMEKV(J,YD,XD,D,GW3, -1,0,INDFIX,KFIX,KM,SKD,D,SIGD,VIA) END;

```

```

FOR I = (1,1,G23) DO Ø[I] = KD[I];
L3: J2 = 0;
FOR I = (1,1,NP) DO BEGIN
  M = C[3,I];
  S = C[5,I]/C[6,I];
  IF M GTR 0 AND S NEQ 0 AND J GEQ GW3 THEN BEGIN
    H = C[4,I];
    Q = C[1,I];
    FBISS = C[2,I];
    DR = FKT(GW1,GW2,GW3,KK,H);
    CR = FKT(0,GW3,GW3,KM,H);
    BR = IF FBISS EQL 0 THEN 0 ELSE CR/FBISS *
      FKT(0,GW3,GW3,KQ,H);
    AR = 1 - BR/CR * DR;
    DP = S;
    CP = M;
    BP = IF FBISS EQL 0 THEN 0 ELSE M * Q/FBISS;
    AP = 1 - BP/M * S;
    EKTVA(CP * BR - CR * BP, DR * BP + CP * AR - DP * BR - AP * CR,
      DR * AP - DP * AR, X1, X2, IMA);
    FDE = FKT(G21,G22,G23,KD,H);
    Q = (S - M * FDE)/(DR - CR * FDE);
    J2 = J2 + 1;
    YD[J2] = X2;
    D[J2] = ABS((S + DR * Q)/(M - CR * Q));
    FOR I1 = (1,1,G22) DO XD[I1,J2] = H ** (G21 + I1 -1);
    FOR I1 = (G22 + 1,1,G23) DO XD[I1,J2] = -X2 * H ** (I1 - G22);

```

```

IMA:      END END;

IF K[NR,2,0] LEQ 0 AND   -K[NR,2,0] LSS G23 AND
J2 GEQ G23 THEN BEGIN

    INDFIX[0] = NFIX = -K[NR,2,0];

    FOR I = (1,1,NFIX) DO BEGIN
        INDFIX[I] = P[NR,2,I];
        KFIX[I] = KD[INDFIX[I]] END;

    SIGD = 1;

    MKMEKV(J2,YD,XD,D,G23,0,NFIX,INDFIX,KFIX,KD,SKD,YQ,SIGD,VIA);

    SUMMA = 0;

    FOR I = (1,1,G23) DO BEGIN
        IF KD[I] NEQ 0 THEN
            SUMMA = SUMMA + ABS(Ø[I]/KD[I] -1);
            Ø[I] = KD[I] END;

    IF CLOCK - TID1 GTR 10 THEN BEGIN

        EJKLAR = 1;

        WRITE ('TIME EXEDED') END ELSE

        IF SUMMA GTR 110-3 AND EJKLAR GEQ 0 THEN GO TO L3 END

    ELSE FOR I = (1,1,G23) DO SKD[I] = 0;

    FOR I = (1,1,G13) DO KK[I] = KP[I];

L2:  J1 = 0;

    FOR I = (1,1,NP) DO BEGIN
        S = C[5,I]/C[6,I];

        IF S NEQ 0 THEN BEGIN
            H = C[4,I];

            FBISS = C[2,I];

            DP = IF FBISS EQL 0 THEN 0 ELSE C[1,I]/FBISS;

            J1 = J1 +1;

            AP = YP[J1] = 1/(1/(S - FKT(G21,G22,G23,KD,H) *
                                ABS(C[3,I])) - DP);

```

```

D[J1] = ABS(S * (1 + DP * FKT(G11,G12,G13,KP,H)) ** 2);
FOR I1 = (1,1,G12) DO XP[I1,J1] = H ** (G11 + I1 - 1);
FOR I1 = (G12, + 1,1,G13) DO
    XP[I1,J1] = -AP * H ** (I1 - G12) END END;
IF K[NR,1,0] LEQ 0 AND -K[NR,1,0] LSS G13 AND
J1 GEQ G13 THEN BEGIN
    INDFIX[0] = NFIX = -K[NR,1,0];
    FOR I = (1,1,NFIX) DO BEGIN
        INDFIX[I] = P[NR,1,I];
        KFIX[I] = KP[INDFIX[I]] END;
    SIGP = ABS(XSORT[NR])/100;
    MKMEKV(J1,YP,XP,D,G13,0,NFIX,INDFIX,KFIX,KP,SKP,Ø,SIGP,VIA);
    SUMMA = 0;
    FOR I = (1,1,G13) DO BEGIN
        IF KP[I] NEQ 0 THEN
            SUMMA = SUMMA + ABS(KK[I]/KP[I] - 1);
            KK[I] = KP[I] END;
    IF CLOCK - TID1 GTR 10 THEN BEGIN
        EJKLAR = 1;
        WRITE ('TIME EXEDED') END
    ELSE IF SUMMA GTR 110 - 3 AND EJKLAR GEQ 0
        THEN GO TO L2 END
ELSE FOR I = (1,1,G13) DO SKP[I] = 0;

SUMMA = 0;
FOR I = (1,1,G13) DO BEGIN
    IF KP[I] NEQ 0 THEN SUMMA = SUMMA + ABS(K[NR,1,I]/KP[I] - 1);
    K[NR,1,I] = KP[I] END;

```



```

FOR I = (1,1,G23) DO BEGIN
    IF KD[I] NEQ 0 THEN SUMMA = SUMMA + ABS(K[NR,2,I]/KD[I] - 1);
    K[NR,2,I] = KD[I] END;
IF CLOCK - TID1 GTR NP THEN BEGIN
    EJKLAR = 1;
    WRITE ('TIME EXEDED') END
ELSE IF EJKLAR GEQ 0 AND BORT EQL 0
AND SUMMA GTR 110 - 4 AND K[RN,1,0] + K[RN,2,0] LSS 2 THEN BEGIN
    VARV = VARV + 1;
    GO TO L1 END;

J = 0;
FOR I1 = G13,G23 DO BEGIN
    J = J + 1;
    I = 0;
    TFAK[J,0] = 1;
    JO = IF I1 EQL G13 THEN J1 ELSE J2;
    FOR A = 0.6827, 0.9, 0.95, 0.99 DO BEGIN
        I = I + 1;
        TFAK[J,I] = IF JO - I1 LEQ 0 THEN 0
                    ELSE TF(JO,I1,A) END END;
WRITE (LUT5);
J = 0;
SYNT = 0;
ISORT = XSORT[NR];
IF BORT EQL 0 AND XNEG[NR] EQL XNEG[RN] THEN BEGIN
    N = ABS(DIAG[NR]);
    IF N GEQ 10 THEN BEGIN
        W = IF N GEQ 20 THEN 2 ELSE 1;
        DIAG[NR] = (N - 10 * W) * SIGN(DIAG[NR]) END END;

```

```

FOR I = (1,1,NP) DO BEGIN
  D[I] = H = C[4,I];
  A = C[5,I];
  Q = C[6,I];
  M = ABS(C[3,I]);
  FPRIM = FKT (G11,G12,G13,KP,H);
  FBISS = C[2,I];
  S = 1+ IF FBISS EQL 0 THEN 0 ELSE FPRIM/FBISS * C[1,I];
  FDE = FKT (G21,G22,G23,KD,H);
  KOB = (FPRIM/S + FDE * M) * Q;
  SYNT = SYNT + IF KOB LEQ 0 THEN 0 ELSE
    ABS(A/KOB - 1) ** 2;
  FDK = (A/Q - FPRIM/S)/M;
  FPK = 1/(1/(A/Q - FDE * M) - IF FBISS EQL 0 THEN 0
    ELSE C[1,I]/FBISS);
  YD[I] = IF W EQL 1 THEN FPK ELSE FDK;
  IF STK[NR,1] EQL STK[NR,2] THEN WRITE (LUT6);
  IF ISORT GTR 0 THEN BEGIN
    IF ABS(A/KOB -1) GEQ ISORT/100 AND
      KOB GTR 0 THEN BEGIN
      J = J + 1;
      SORT[J] = I END END END;
  SIGMA[NR] = SQRT(SYNT/(NP - 1));
  WRITE (SIGMA[NR] * 100);
  IF STK[NR,2] NEQ 0 THEN SIGXX[NR] = SIGMA[NR];

  IF J GTR 0 AND NP - J GTR G13 + G23 THEN BEGIN
    BORT = BORT + J;
    WRITE (FOR I = (1,1,J) DO C[9,SORT[I]]);
    FOR I = (1,1,J) DO C[4,SORT[I]] = 0;
    J1 = 0;
  
```

```

FOR I = (1,1,NP) DO IF C[4,I] NEQ 0 THEN BEGIN
    J1 = J1 + 1;
    IF J1 NEQ I THEN FOR I1 = (1,1,9) DO
        C[I1,J1] = C[I1,I] END;
    IF NR EQL SYSTNR THEN BEGIN
        SYSTDATA = NP - J;
        FOR J = (1,1,9) DO FOR I = (1,1,SYSTDATA) DO
            CSYST[J,I] = C[J,I] END
    ELSE BEGIN
        REFDATA = NP - J;
        FOR J = (1,1,9) DO FOR I = (1,1,REFDATA) DO
            CREF[J,I] = C[J,I] END END;

    IF BORT EQL 0 AND XNEG[NR] EQL XNEG[RN] THEN BEGIN
        IF AFORM EQL 1 AND DIAG[NR] NEQ 0 THEN BEGIN
            FOR I = (1,1,10) DO KK[I] =
                IF W EQL 1 THEN KP[I] ELSE KD[I];
            RITA (DIAG[NR],D,YD,NP,FKT,G[NR,W,1],G[NR,W,2],
                G[NR,W,3],KK);
            DIAG[NR] = 0 END END;

        IF VARV NEQ 0 THEN BEGIN
            WRITE(VARV);
            EJKLAR = -EJKLAR;
            VARV = 0;
            GO TO L1 END;

        IF BORT GTR 0 THEN BEGIN
            NR = RN;
            IF K[NR,1,0] + K[NR,2,0] LSS 2 THEN VARV = 1;
            GO TO LO END END;

```

```
FOR I = NR,RN DO XSORT[I] = -ABS(XSORT[I]);
```

```
N = W;
```

```
IF XNEG[NR] NEQ XNEG[RN] THEN BEGIN
```

```
  FOR J = NR,RN DO FOR I = N, IF W EQL 1 THEN 2
```

```
  ELSE 1 DO BEGIN
```

```
    GW3 = G[J,I,3];
```

```
    W = K[J,I,0];
```

```
    IF W LSS 1 THEN FOR I1 = (GW3,-1,1) DO
```

```
    IF K[J,I,I1] LSS 0 THEN BEGIN
```

```
      K[J,I,I1] = 0;
```

```
      K[J,I,0] = W = W-1; P[J,I, - W] = I1;
```

```
      IF W + GW3 EQL 0 THEN K[J,I,0] = 1;
```

```
      NR = RN;
```

```
      IF K[NR,1,0] + K[NR,2,0] LSS 2 THEN VARV = 1;
```

```
      GO TO LO END END;
```

```
    XNEG[NR] = XNEG[RN] = 0 END;
```

```
  K[NR,1,0] = K[NR,2,0] = K[RN,1,0] = K[RN,2,0] = 1;
```

```
  STK[NR,2] = STK[RN,2] = 0;
```

```
  IF STK[SYSTNR,1] GTR 0 THEN FOR I = (1,1,SYSTDATA) DO
```

```
  BEGIN HFAK = STK[SYSTNR,3]/1000;
```

```
    KFAK = STK[SYSTNR,4]/1000;
```

```
    IF HFAK GTR 0 THEN CSYST[4,I] = CSYST[8,I] * (1 + SLUMP * HFAK)
```

```
    IF KFAK GEQ 0 THEN CSYST[5,I] = CSYST[7,I] * (1 + SLUMP *
```

```
      IF KFAK GTR 0 THEN KFAK ELSE SIGXX[SYSTNR]) END;
```

```
  IF STK[REFNR,1] GTR 0 THEN FOR I = (1,1,REFDATA) DO
```

```
  BEGIN HFAK = STK[REFNR,3]/1000;
```

```
    KFAK = STK[REFNR,4]/1000;
```

```
    IF HFAK GTR 0 THEN CREF[4,I] = CREF[8,I] * (1 + SLUMP * HFAK);
```

```

      IF KFAK GEQ 0 THEN CREF[5,I] = CREF[7,I] * (1 + SLUMP *
      IF KFAK GTR 0 THEN KFAK ELSE SIGXX[REFNR]) END;

SYNT = 0;

FOR I1 = NR,RN DO IF STK[I1,1] GTR 0 THEN BEGIN
    STK[I1,1] = STK[I1,1] -1;
    IF STK[I1,1] LEQ 0 THEN STK[I1,2] = 1;
    SYNT = SYNT + 1;
    FOR J = 1,2 DO BEGIN
        I = 0;
        K[I1,J,0] = 0;
        FOR I = I + 1 WHILE P[I1,J,I] NEQ 0 DO
            K[I1,J,0] = -I END END;
    IF SYNT NEQ 0 THEN BEGIN
        NR = RN;
        GO TO LO END;

SLUT:      GO TO KORT2 END END;

UTHOPP:    END END

```